Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Amine-catalyzed cascade reactions of ketoses with 1.3-dicarbonyl compounds

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Table of contents

1. General

^{1}H-NMR, ^{13}C-NMR, DEPT and correlation experiments H, H-COSY, HSQC, NOESY and JRES were carried out at 600, 500 MHz and 125 MHz respectively using a Bruker Avance-300 or Bruker-500 spectrometer. The residual protonated solvent was used as the internal standard:

^{1}H-NMR: 7.26 ppm for $CDCl_3$, ^{13}C-NMR: 77.0 ppm for $CDCl_3$,

^{1}H-NMR: 3.31 ppm for MeOD, ^{13}C-NMR: 49.0 ppm for MeOD and

^{1}H-NMR: 2.05 ppm for acetone-d_6, ^{13}C-NMR: 206.3 / 29.8 ppm for acetone-d_6.

Chemical shifts are given in ppm, coupling constants in Hz. Multiplicity is as follows: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet.

High resolution mass spectroscopy was performed out on a LTQ-FT-ICR machine (Finnigan) (ESI).

Optical rotation values were measured with a JASCO DIP-370 polarimeter.

Purification of products was accomplished by flash chromatography (Merck silica gel 60, particle size 0.04 - 0.063 mm). Yields were determined after column chromatography. The solvent mixtures of

CH_2Cl_2 (DCM) and methanol in ratio 80/20 → 95/5 and

hexane/acetone 7/3 → 1/1 and

hexane/ ethyl acetate 6/4 → 4/6 were used as eluent.

Thin layer chromatography was performed with Merck Silica Gel 60 F_{254} TLC plates. Development was performed with cer(IV) sulfate / phosphormolybdic acid. The solvent mixture of DCM and methanol was applied in ratio of 90 / 10.

Solvents were purchased from Sigma-Aldrich or Merck and used – if not mentioned - without further purification or drying.

Carbohydrates were used as purchased (TCI, Sigma).

2. General procedures

General procedure A: for ketones **3**, **4**, **6** and **7**

In a snap cap vial 8.0 mmol (2.0 eq) ketone, 4.0 mmol (1.0 eq) 1.3-dicarbonyl compound and 122 mg (0.8 mmol, 0.2 eq) DBU were solved in 2.0 ml water and stirred at room temperature for 24-96 hours (DC-control). The raw product was directly purified by column chromatography.

General procedure B: for ketose **9**

In a snap cap vial 4.0 mmol (1.0 eq) ketose, 8.0 mmol (2.0 eq) 1,3-dicarbonyl compound and 4.0 mmol (1.0 eq) DBU were solved in 2.0 ml water and stirred at room temperature for 48 hours (DC-control). The raw product was directly purified by column chromatography.

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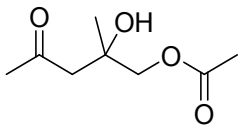
General procedure B: for acetylated ketoses **13**-**18**

In a snap cap vial 4.0 mmol (1.0 eq) ketose, 8.0 mmol (2.0 eq) 1,3-dicarbonyl compound and 4.0 mmol (1.0 eq) DBU were solved in 2.0 ml water and stirred at room temperature for 8 days. After removal of water under reduced pressure the remaining crude reaction mixture was acetylated with dry pyridine and acetic anhydride at r.t. The reaction mixture was quenched with 100.0 mL of aqueous saturated Na_2CO_3 –solution. The aqueous phase was extracted three times with each 100.0 mL of ethyl acetate. The combined organic phase was washed with 100.0 mL of aqueous saturated NH_4Cl-solution and 100.0 mL of brine. The separated organic layer was dried ($MgSO_4$) and evaporated i. vac. The crude residue was purified by column chromatography

3. Characterization of compounds

rac-2-Hydroxy-2-methyl-4-oxopentyl acetate (**3a**)



Yield: 83 %

R_f = 0,57 (hexane / acetone: 1 / 1)

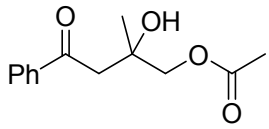
^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.04 (s, 1H), 4.00 (d, *J* = 11.2 Hz, 1H), 3.92 (d, *J* = 11.2 Hz, 1H), 2.72 (d, *J* = 17.3 Hz, 1H), 2.54 (d, *J* = 17.3 Hz, 1H), 2.15 (s, 3H), 2.04 (s, 3H), 1.20 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ = 210.2, 170.9, 70.8, 70.2, 49.4, 31.8, 24.8, 20.9.

HRMS calcd for $C_8H_{14}O_4$ $[M+Na]^+$: 197,0784 found: 197,0782

$[M+K]^+$: 213,0524 found: 213,0521

rac-2-hydroxy-2-methyl-4-oxo-4-phenylbutyl acetate (**3b**)



The products **3b** and **4b** were isolated as inseparable mixtures (**3b**/**4b**: 71/29).

Yield: 64 %

R_f = 0,41 (hexane / acetone: 7 / 3)

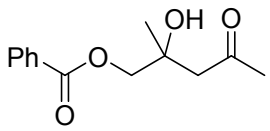
^{1}H NMR (500 MHz, acetone-d_6) δ = 8.05 – 8.02 (m, 2H), 7.54 – 7.49 (m, 3H), 4.32 (s, 1H), 4.12 (d, *J* = 10.9 Hz, 1H), 4.08 (d, *J* = 10.9 Hz, 1H), 3.36 (d, *J* = 16.1 Hz, 1H), 3.22 (d, *J* = 16.1 Hz, 1H) 1.96 (s, 3H), 1.34 (s, 3H).

^{13}C NMR (125 MHz, acetone-d_6) δ = 200.7, 170.8, 138.7, 134.0, 129.4, 129.1, 71.6, 71.0, 45.8, 25.3, 20.7.

HRMS calcd for $C_{13}H_{16}O_4$ [M+Na] : 259,0941 found: 259,0942

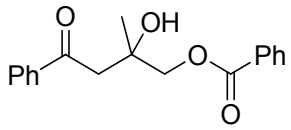
$[M+K]^+$: 275,0680 found: 275,0683

rac-2-hydroxy-2-methyl-4-oxopentyl benzoate (**4b**)



^{1}H NMR (500 MHz, acetone-d_6) δ = 8.09 – 8.06 (m, 2H), 7.66 – 7.60 (m, 3H), 4.40 (s, 1H), 4.28 (d, J= 11.0 Hz, 1H), 4.25 (d, *J* = 11.0 Hz, 1H), 2.88 (d, *J* = 15.7 Hz, 1H), 2.78 (d, *J* = 15.7 Hz, 1H), 2.19 (s, 3H), 1.34 (s, 3H).
^{13}C NMR (125 MHz, acetone-d_6) δ = 209.1, 166.5, 133.9, 131.1, 130.3, 129.3, 71.5, 71.2, 51.1, 32.1, 25.1.

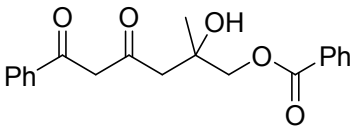
rac-2-hydroxy-2-methyl-4-benzoyl-butyl benzoate (**3c**) [1]



Yield: 8 %
R_f = 0,64 (hexane / acetone: 7 / 3)
^{1}H NMR (500 MHz, acetone-d_6) δ = 8.07 – 8.02 (m, 4H), 7.63 – 7.58 (m, 2H), 7.51 – 7.45 (m, 4H), 4.53 (s, 1H), 4.41 (d, *J* = 10.9 Hz, 1H), 4.38 (d, *J* = 10.9 Hz, 1H), 3.50 (d, *J* = 16.1 Hz, 1H), 3.36 (d, *J* = 16.1 Hz, 1H), 1.46 (s, 3H).
^{13}C NMR (125 MHz, acetone-d_6) δ = 200.7, 166.5, 138.6, 134.0, 133.8, 131.1, 130.2, 129.4, 129.3, 129.1, 71.7, 71.7, 46.0, 25.5.
HRMS calcd. for $C_{18}H_{18}O_4$ $[M+H]^+$: 299,1283 found: 299,1280
$[M+Na]^+$: 321,1103 found: 321,1099
$[M+K]^+$: 337,0842 found: 337,0839

rac-2-hydroxy-2-methyl-4,6-dioxo-6-phenylhexyl benzoate (**3d**)

Mixture of keto-enol form (keto/enol**:** 58/42).



Yield: 29 %

R_f = 0,4 (hexane / acetone: 7 / 3)

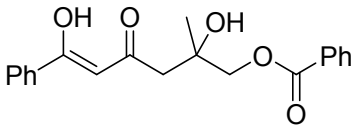
^{1}H NMR (300 MHz, acetone-d_6) δ = 8.13 – 8.04 (m, 2H), 7.56 – 7.44 (m, 8H), 4.26 (d, *J* = 10.8 Hz, 1H), 4.19 (d, *J* = 10.8 Hz, 1H), 3.34 (d, *J* = 16.4 Hz, 1H), 3.19 (d, *J* = 16.4 Hz, 1H), 2.09 (s, 2H), 1.32 (s, 3H).

^{13}C NMR (75 MHz, acetone-d_6) δ = 195.5, 193.7, 168.0, 138.5, 134.0, 133.4, 131.0, 130.3, 129.6, 129.3, 129.1, 71.5, 71.4, 48.7, 46.2, 25.2.

HRMS calcd for $C_{20}H_{20}O_5$ $[M-H]^-$: 339.1238 found: 339.1236

$[M+Cl]^-$. 375.1005 found: 375.1004

enolstructure of 2-hydroxy-2-methyl-4,6-dioxo-6-phenylhexyl benzoate (**3d**)

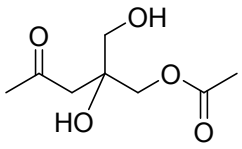


^{1}H NMR (300 MHz, acetone-d_6) δ = 8.03 – 7.96 (m, 4H), 7.93 – 7.89 (m, 2H), 7.66 – 7.57 (m, 4H), 6.56 (s, 1H), 4.45 (s, 1H), 4.35 (d, *J* = 0.6 Hz, 1H), 4.15 (s, 2H), 2.86 (d, *J* = 1.0 Hz, 2H), 1.46 (s, 3H).

^{13}C NMR (75 MHz, acetone-d_6) δ = 200.6, 184.0, 166.5, 137.0, 134.4, 133.9, 130.3, 129.5, 129.3, 129.3, 127.8, 99.2, 71.9, 71.8, 45.6, 25.3.

rac-2-hydroxy-2-(hydroxymethyl)-4-oxopentyl acetate (**6a**)

inseperable mixture of **6a**, **7a** and **7b** (55 / 25 / 20).



Yield: 72 %

R_f = 0,72 (DCM : methanol / 8 : 2)

^{1}H NMR (500 MHz, acetone-d_6) δ = 4.29 (s, 1H), 4.07 (d, *J* = 11.2 Hz, 1H), 4.03 (d, *J* = 11.2 Hz, 1H), 3.98 (t, *J* = 5.3 Hz, 1H), 3.50 (d, *J* = 5.1 Hz, 2H), 2.73 (d, *J* = 15.7 Hz, 1H), 2.68 (d, *J* = 15.7 Hz, 1H), 2.18 (s, 3H), 2.00 (s, 3H).

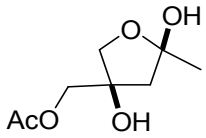
^{13}C NMR (125 MHz, acetone-d_6) δ = 209.7, 171.0, 73.9, 67.2, 65.9, 46.4, 32.2, 20.7.

HRMS calcd. for $C_8H_{14}O_5$ $[M+Na]^{+:}$ 213,0733 found: 213,0734

$[M+Cl]^-$: 225.0535 found: 225.0533

$[M+K]^+$: 229,0473 found: 229,0475

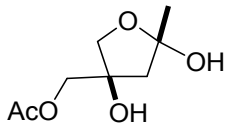
rac-[(3R,5R)-3,5-dihydroxy-5-methyloxolan-3-yl]methyl acetate (**7a**)



^{1}H NMR (500 MHz, acetone-d_6) δ = 4.89 (s, 1H), 4.59 (s, 1H), 4.10 (d, *J* = 11.3 Hz, 1H), 4.05 (d, *J* = 11.3 Hz, 1H), 3.90 (d, *J* = 9.3 Hz, 1H), 3.85 (d, *J* = 9.3 Hz, 1H), 2.02 (s, 3H), 2.00 (m, 2H), 1.41 (s, 3H).

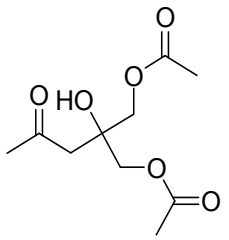
^{13}C NMR (125 MHz, acetone-d_6) δ = 171.1, 106.1, 80.4, 76.2, 68.3, 48.7, 26.8, 20.7.

rac-[(3R,5S)-3,5-dihydroxy-5-methyloxolan-3-yl]methyl acetate (**7b**)



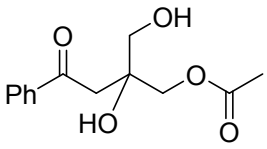
^{1}H NMR (500 MHz, acetone-d_6) δ = 4.65 (s, 1H), 4.23 (s, 1H), 4.17 (d, *J* = 11.2 Hz, 1H), 4.15 (d, *J* = 11.2 Hz, 1H), 3.96 (d, *J* = 9.3 Hz, 1H), 3.72 (d, *J* = 9.3 Hz, 1H), 2.14 (d, *J* = 13.6 Hz, 1H), 2.01 (s, 3H), 1.96 (d, *J* = 13.6 Hz, 1H), 1.49 (s, 3H).
^{13}C NMR (125 MHz, acetone-d_6) δ = 171.2, 106.0, 80.5, 75.9, 69.5, 50.4, 28.0, 20.7.

4,5-diacetoxy-4-(hydroxymethyl)pentan-2-one (diacetate of **6a**)



Yield: 72 %
^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.34 (s, 1H), 4.08 (s, 4H), 2.70 (s, 2H), 2.21 (s, 3H), 2.07 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$) δ = 209.7, 170.7, 72.1, 66.5, 44.9, 31.8, 20.9.
HRMS calcd. for $C_{10}H_{16}O_6$ $[M+H]^+$: 233,1020 found: 233,1021
$[M+Na]^+$: 255,0839 found: 255,0839

rac-2-hydroxy-2-(hydroxymethyl)-4-oxo-4-phenylbutyl acetate (**6b**)



Yield: 75 %

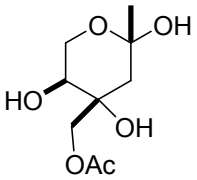
R_f = 0,75 (DCM : methanol / 8 : 2)

^{1}H NMR (500 MHz, acetone-d_6) δ = 8.05 – 8.03 (m, 2H), 7.65 – 7.60 (m, 1H), 7.54 – 7.49 (m, 2H), 4.45 (s, 1H), 4.23 (d, *J* = 11.2 Hz, 1H), 4.18 (d, *J* = 11.2 Hz, 1H), 4.08 (t, *J* = 6.0 Hz, 1H), 3.66 (d, *J* = 5.8 Hz, 2H), 3.32 (s, 2H), 1.95 (s, 3H).

^{13}C NMR (125 MHz, acetone-d_6) δ = 201.0, 171.0, 138.6, 134.0, 129.3, 129.1, 74.5, 67.5, 66.1, 41.3, 20.6.

HRMS calc. $C_{13}H_{16}O_5$	$[M+H]^+$: 253,1076	found: 253,1070
	$[M+Na]^+$: 275,0890	found: 275,0891
	$[M+K]^+$: 291,0629	found: 291,0631

((2S,4S,5S)-tetrahydro-2,4,5-trihydroxy-2-methyl-2H-pyran-4-yl)methyl acetate (**9**)



Yield: 22 %

R_f = 0,38 (DCM : methanol / 8 : 2)

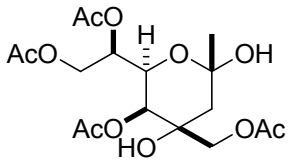
$[\alpha]_D^{25°C}$ = - 1.2 (c = 1, acetone)

^{1}H NMR (500 MHz, MeOD-d_4) δ = 4.04 (d, J = 11.1 Hz, 1H), 4.01 (d, J = 11.1 Hz, 1H), 3.83 (t, J = 10.9 Hz, 1H), 3.63 (dd, J = 11.0, 5.6 Hz, 1H), 3.54 (dd, J = 11.0, 5.6 Hz, 1H), 2.08 (s, 3H), 1.91 (d, J = 14.2 Hz, 1H), 1.72 (d, J = 14.2 Hz, 1H), 1.33 (s, 3H).

^{13}C NMR (125 MHz, MeOD-d_4) δ = 172.5, 97.3, 73.1, 68.0, 67.3, 60.8, 41.5, 28.8, 20.8.

HRMS calcd. for $C_9H_{16}O_6$	$[M+Na]^+$: 243,0839	found: 243,0836
	$[M+K]^+$: 259,0578	found: 295,0576
	$[M+NH_4]$: 238,1285	found: 238,1282

((2S,4R,5S,6R)-tetrahydro-2,4-trihydroxy-5-acetoxy-6-((R)-1,2-diacetoxyethyl)-2-methyl-2H-pyran-4-yl)methyl acetate (**13**)



Yield: 39 %

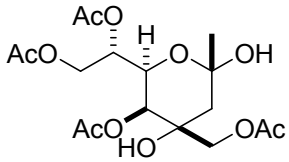
$[\alpha]_D^{25°C}$ = + 41.7 (c = 1, acetone)

^{1}H NMR (500 MHz, acetone-d_6) δ = 5.90 (s, 1H), 5.32 (s, 1H), 5.01 (s, 1H), 4.99 (ddd, J = 9.6, 5.9, 2.5 Hz, 1H), 4.52 (dd, J = 9.7, 1.5 Hz, 1H), 4.45 (dd, J = 12.0, 2.4 Hz, 1H), 4.08 (d, J = 11.5 Hz, 1H), 4.08 (dd, J = 12.1, 5.8 Hz, 1H), 3.72 (d, J = 11.5 Hz, 1H), 1.98 (s, 3H), 1.98 (s, 3H), 1.97 (s, 3H), 1.96 (s, 3H), 1.81 (s, 2H), 1.40 (s, 3H).

^{13}C NMR (125 MHz, acetone-d_6) δ = 170.8, 170.8, 170.4, 170.3, 97.5, 72.2, 69.1, 68.0, 67.1, 66.4, 63.6, 37.3, 29.1, 21.0, 20.9, 20.7, 20.6**.**

HRMS calcd. for $C_{17}H_{26}O_{11}$	$[M+Na]^+$: 429.1367	found: 429.1369
	$[M+K]^+$: 445.1107	found: 445.1111
	$[M+NH_4]^+$: 466.1919	found: 466.1918
	$[M-H]^-$: 405.1402	found: 405.1400

((2S,4R,5S,6R)-tetrahydro-2,4-trihydroxy-5-acetoxy-6-((S)-1,2-diacetoxyethyl)-2-methyl-2H-pyran-4-yl)methyl acetate (**14**)



Yield: 34 %

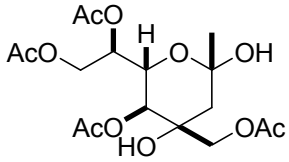
^{1}H NMR (500 MHz, acetone-d_6) δ = 5.85 (d, J = 0.8 Hz, 1H), 5.30 (s, 1H), 5.17 (ddd, J = 7.7, 6.8, 3.1 Hz, 1H), 4.98 (s, 1H), 4.56 (dd, J = 7.7, 1.3 Hz, 1H), 4.36 (dd, J = 12.1, 3.1 Hz, 1H), 4.10 (d, J = 11.5 Hz, 1H), 4.03 (dd, J = 12.1, 6.8 Hz, 1H), 3.71 (d, J = 11.5 Hz, 1H), 2.10 (s, 3H), 2.00 (s, 3H), 1.98 (s, 3H), 1.98 (s, 3H), 1.84 (dd, J = 14.0 Hz, 1.1 Hz 1H), 1.77 (dd, J = 14.0, 1.1 Hz, 1H), 1.40 (s, 3H).

^{13}C NMR (125 MHz, acetone-d_6) δ = 170.8, 170.7, 170.4, 97.3, 72.5, 71.4, 68.3, 67.9, 66.7, 63.1, 37.3, 29.2, 21.1, 20.9, 20.7, 20.6**.**

HRMS calcd. for $C_{17}H_{26}O_{11}$	$[M+Na]^+$: 429.1367	found: 429.1366
	$[M+K]^+$: 445.1107	found: 445.1107

	$[M+NH_4]^+$: 466.1919	found: 466.1916
	$[M-H]^-$: 405.1402	found: 405.1400

((2R,4R,5S,6S)-tetrahydro-2,4-dihydroxy-5-acetoxy-6-((R)-1,2-diacetoxyethyl)-2-methyl-2H-pyran-4-yl)methyl acetate (**15**)



Yield: 33 %

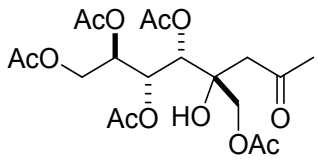
$[\alpha]_D^{25°C}$ = - 17.2 (c = 1, acetone)

^{1}H NMR (500 MHz, acetone-d_6) δ = 5.83 (s, 1H), 5.30 (ddd, J = 8.4, 4.1, 2.4 Hz, 1H), 5.12 (s, 1H), 4.94 (d, J = 10.2 Hz, 1H), 4.40 (dd, J = 10.2, 2.4 Hz, 1H), 4.29 (dd, J = 11.7, 4.1 Hz, 1H), 4.11 (dd, J = 11.7, 8.4 Hz, 1H), 3.96 (d, J = 11.3 Hz, 1H), 3.69 (d, J = 11.3 Hz, 1H), 2.01 (s, 3H), 1.98 (s, 3H), 1.98 (s, 3H), 1.95 (s, 3H), 1.92 (d, J = 14.2 Hz, 1H), 1.38 (s, 3H). (dublett at 1.99 ppm (J = 14.2 Hz) only visible in HSQC).

^{13}C NMR (125 MHz, acetone-d_6) δ = 170.8, 170.8, 170.6, 170.5, 97.6, 73.2, 68.7, 68.7, 67.4, 66.9, 64.0, 42.0, 28.7, 20.9, 20.7, 20.7, 20.6**.**

HRMS calcd. for $C_{17}H_{26}O_{11}$	$[M+Na]^+$: 429.1367	found: 429.1368
	$[M+K]^+$: 445.1107	found: 445.1110
	$[M+NH_4]^+$: 466.1919	found: 466.1916
	$[M-H]^-$: 405.1402	found: 405.1402

(4R,5S,6R,7R)-4,5,6,7,8-pentaacetoxy-4-(hydroxymethyl)octan-2-one (**16**)



Yield: 39 %

$[\alpha]_D^{25°C}$ = + 33.9 (c = 1, acetone)

^{1}H NMR (500 MHz, acetone-d_6) δ = 5.56 (dd, J = 7.1, 2.8 Hz, 1H), 5.39 (d, J = 2.8 Hz, 1H), 5.09 (ddd, J = 7.1, 6.1, 3.0 Hz, 1H), 4.90 (s, 1H), 4.26 (dd, J = 12.3, 3,1 Hz, 1H), 4.12 (d, J = 11.6 Hz, 1H), 4.08 (dd, J = 12.3, 6.1 Hz, 1H), 4.05 (d, J = 11.5 Hz,

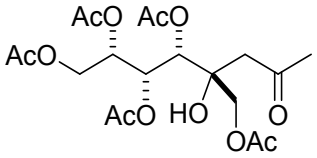
1H), 2.91 (d, J = 16.9 Hz, 1H), 2.80 (d, J = 16.9 Hz, 1H), 2.17 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H).

^{13}C NMR (125 MHz, acetone-d_6) δ = 209.7, 170.8, 170.8, 170.7, 170.4, 170,4, 74.8, 72.1, 70.0, 68.8, 66.7, 62.3, 45.7, 31.8, 21.0, 20.8, 20.7, 20.6, 20.6

HRMS calcd. for $C_{19}H_{28}O_{12}$ $[M+Na]^+$: 471.1473 found: 471.1474

$[M+K]^+$:487.1212 found: 487.1211

(4R,5S,6R,7S)-4,5,6,7,8-pentaacetoxy-4-(hydroxymethyl)octan-2-one (**17**)



Yield: 34 %

$[\alpha]_D^{25°C}$ = - 1.4 (c = 1, acetone)

^{1}H NMR (500 MHz, acetone-d_6) δ = 5.64 (dd, J = 5.9, 4.0 Hz, 1H), 5.36 (d, J = 4.0 Hz, 1H), 5.35 (dd, J = 5.9, 1.7 Hz, 1H), 4.81 (s, 1H), 4.28 (dd, J = 12.0, 4,3 Hz, 1H), 4.15 (d, J = 11.6 Hz, 1H), 4.08 – 4.05 (m, 1H), 4.05 (d, J = 11.5 Hz, 1H), 2.90 (d, J = 17.2 Hz, 1H), 2.81 (d, J = 17.2 Hz, 1H), 2.17 (s, 3H), 2.12 (s, 3H), 2.05 (s, 3H), 2.03 (s, 6H), 1.99 (s, 3H).

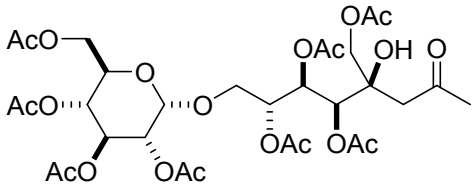
^{13}C NMR (125 MHz, acetone-d_6) δ = 210.0, 170.6, 170.2, 170.2, 74.8, 72.4, 71.1, 69.0, 66.7, 62.6, 45.9, 31.8, 20.8, 20.7, 20.7, 20.6**.**

HRMS calcd. for $C_{19}H_{28}O_{12}$ $[M+Na]^+$: 471.1473 found: 471.1470

$[M+K]^+$: 487.1212 found: 487.1214

$[M+NH_4]^+$: 466.1919 found: 466.1918

(4R,5S,6R,7R)-8-((2S,3R,4S,5S,6R)-tetrahydro-3,4,5-acetoxy-6-(acetoxymethyl)-2H-pyran-2-yloxy)-4-hyroxy-5,6,7-triacetoxy-4-(acetoxymethyl)octan-2-one (**18**)



Yield: 38 %

$[\alpha]_D^{25°C}$ = + 89.3 (c = 1, acetone)

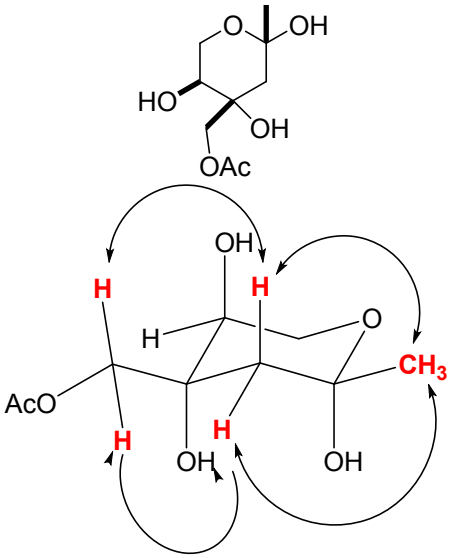
^{1}H NMR (500 MHz, acetone-d_6) δ = 5.61 (dd, J = 6.2, 3.3 Hz, 1H), 5.43 (dd, J = 10.1, 9.5 Hz, 1H), 5.41 (d, J = 3.4 Hz, 1H), 5.21 (td, J = 6.3, 3.5 Hz, 1H), 5.09 (d, J = 3.6 Hz, 1H), 5.03 (dd, J = 10.2, 9.5 Hz, 1H), 4.89 (s, 1H), 4.81 (dd, J = 10.3, 3.6 Hz, 1H), 4.22 (dd, J = 12.3, 5,0 Hz, 1H), 4.17 (d, J = 11.6 Hz, 1H), 4.12 (dd, J = 11.9, 2.8 Hz, 1H), 4.10 (d, J = 11.5 Hz, 1H), 4.05 (ddd, J = 10.3, 4.9, 2.4 Hz, 1H), 3.83 (dd, J = 11.6, 6.3 Hz, 1H), 3.77 (dd, J = 11.6, 3.5 Hz, 1H), 2.92 (d, J = 17.2 Hz, 1H), 2.87 (d, J = 17.2 Hz, 1H), 2.20 (s, 3H), 2.10 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H).

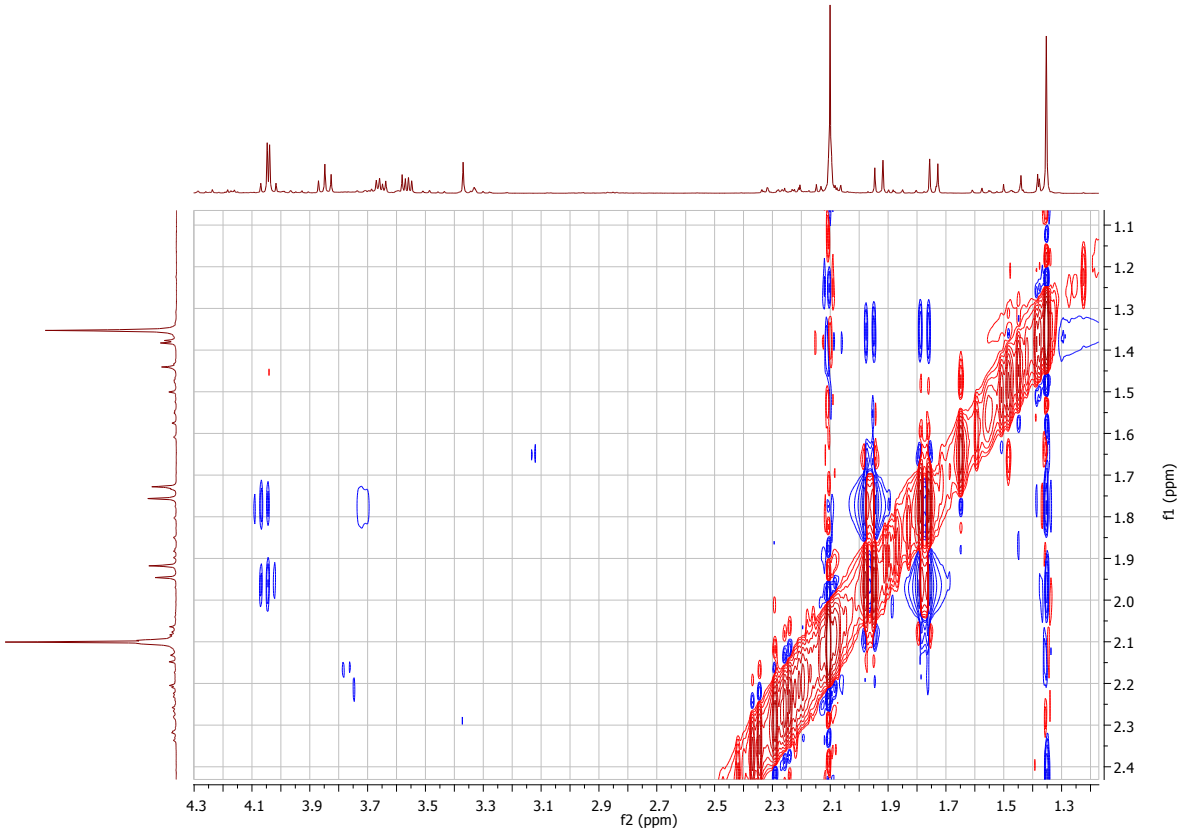
^{13}C NMR (125 MHz, acetone-d_6) δ = 210.0, 170.7, 170.7, 170.5, 170.5, 170.3, 170.2, 170.0, 95.0, 74.9, 72.4, 71.2, 70.5, 70.4, 69.4, 69.3, 68.4, 66.8, 66.1, 62.6, 45.6, 31.8, 21.0, 20.8, 20.7, 20.6, 20.6, 20.6, 20.5, 20.5.

HRMS calcd. $C_{31}H_{44}O_{20}$ $[M+Na]^+$: 759.2318 found: 759.2321

4. Proof of configuration

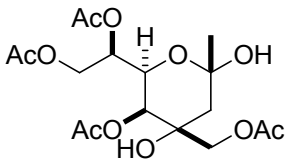
((2S,4S,5S)-tetrahydro-2,4,5-trihydroxy-2-methyl-2H-pyran-4-yl)methyl acetate (**9**) from L-erythrulose

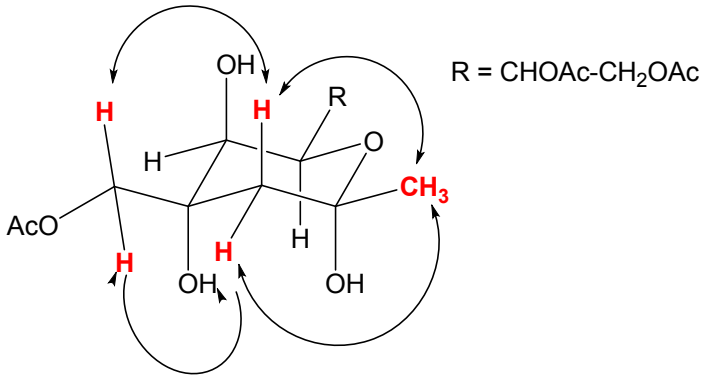




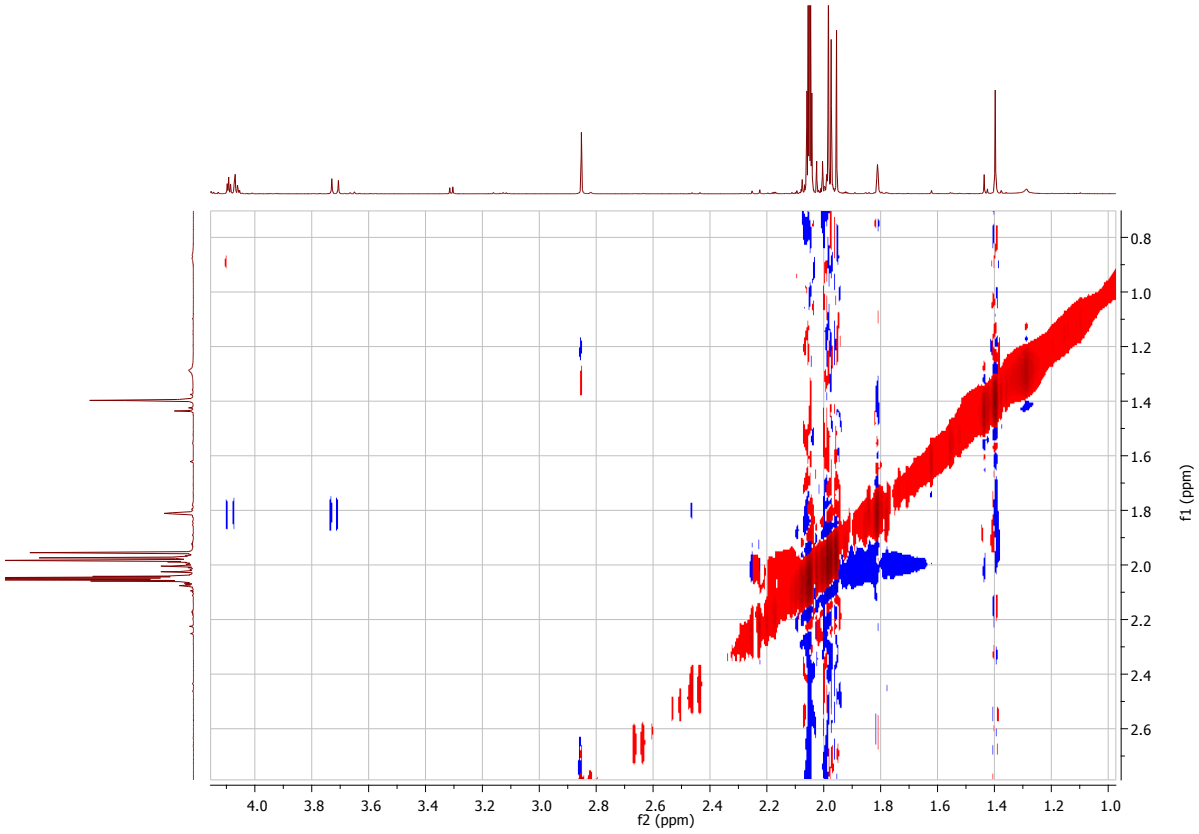
((2S,4R,5S,6R)-tetrahydro-2,4-trihydroxy-5-acetoxy-6-((R)-1,2-diacetoxyethyl)-2-methyl-2H-pyran-4-yl)methyl acetate (**13**)

from D-fructose



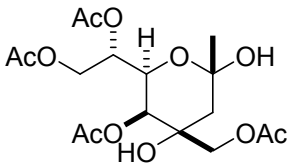


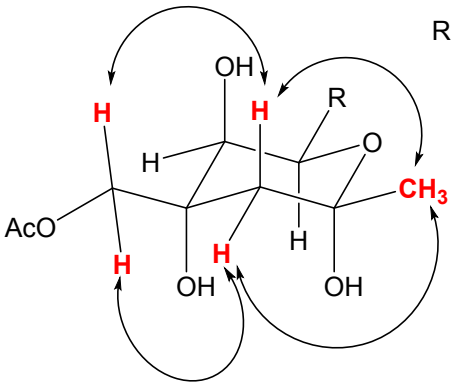
R = CHOAc-CH_2OAc



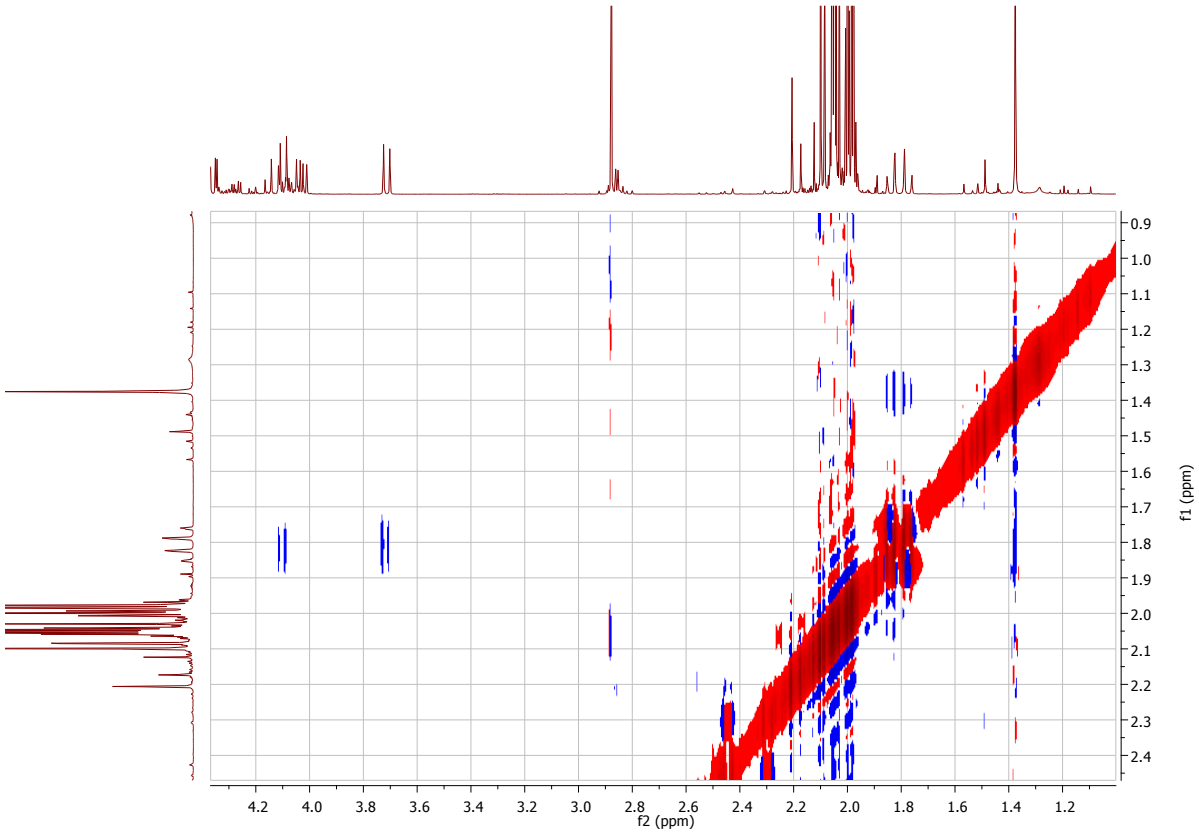
((2S,4R,5S,6R)-tetrahydro-2,4-trihydroxy-5-acetoxy-6-((S)-1,2-diacetoxyethyl)-2-methyl-2H-pyran-4-yl)methyl acetate (**14**)

from L-sorbose



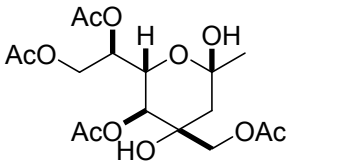


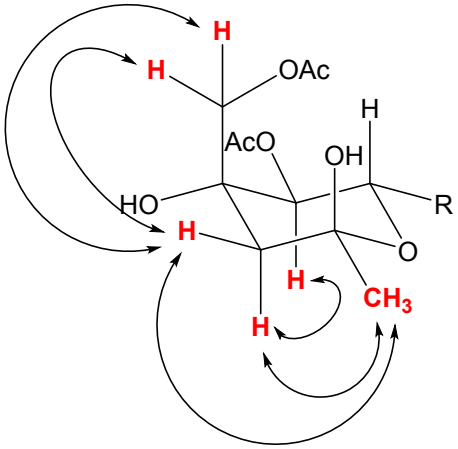
R = CHOAc-CH_2OAc



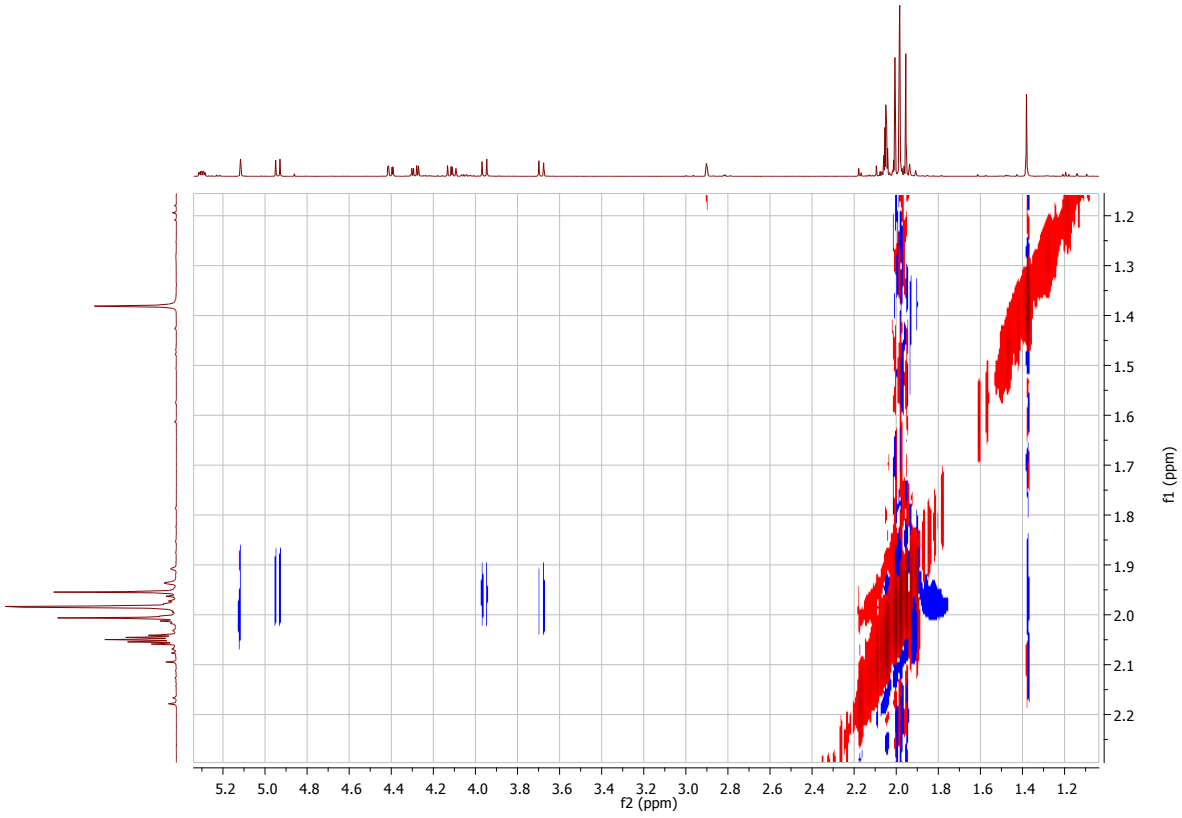
((2R,4R,5S,6S)-tetrahydro-2,4-dihydroxy-5-acetoxy-6-((R)-1,2-diacetoxyethyl)-2-methyl-2H-pyran-4-yl)methyl acetate (**15**)

from D-tagatose



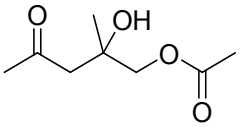


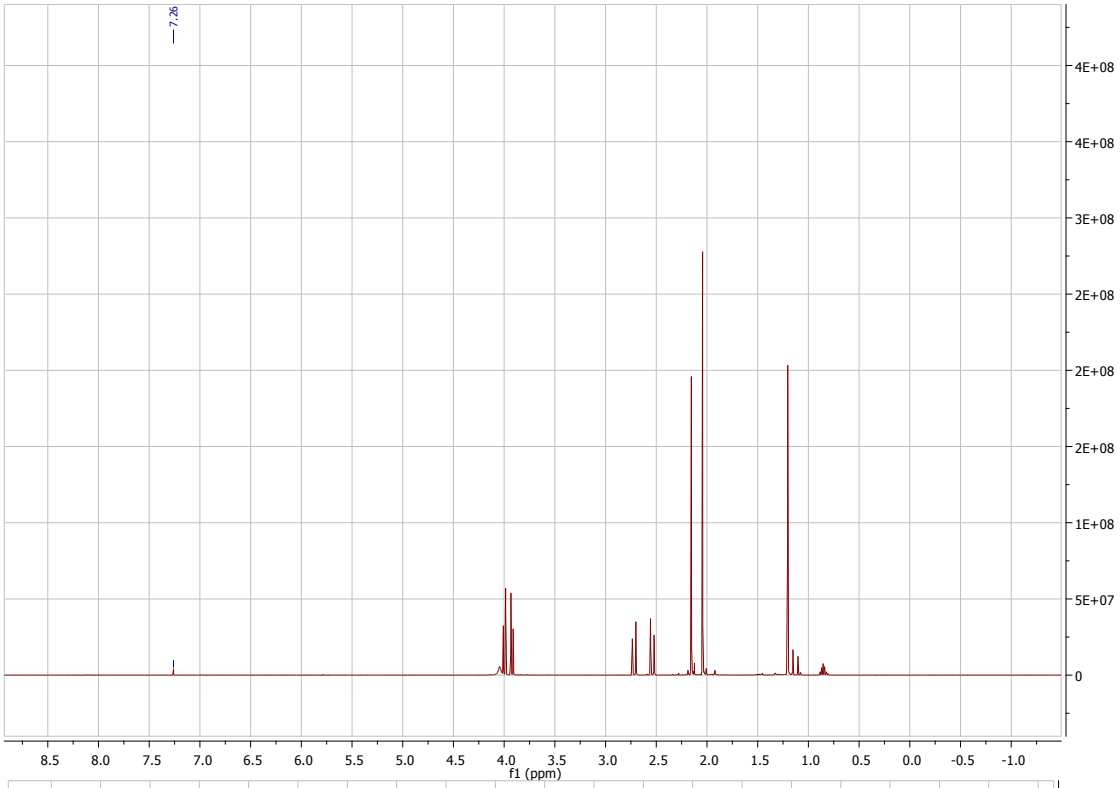
R = $CHOAc\text{-}CH_2OAc$

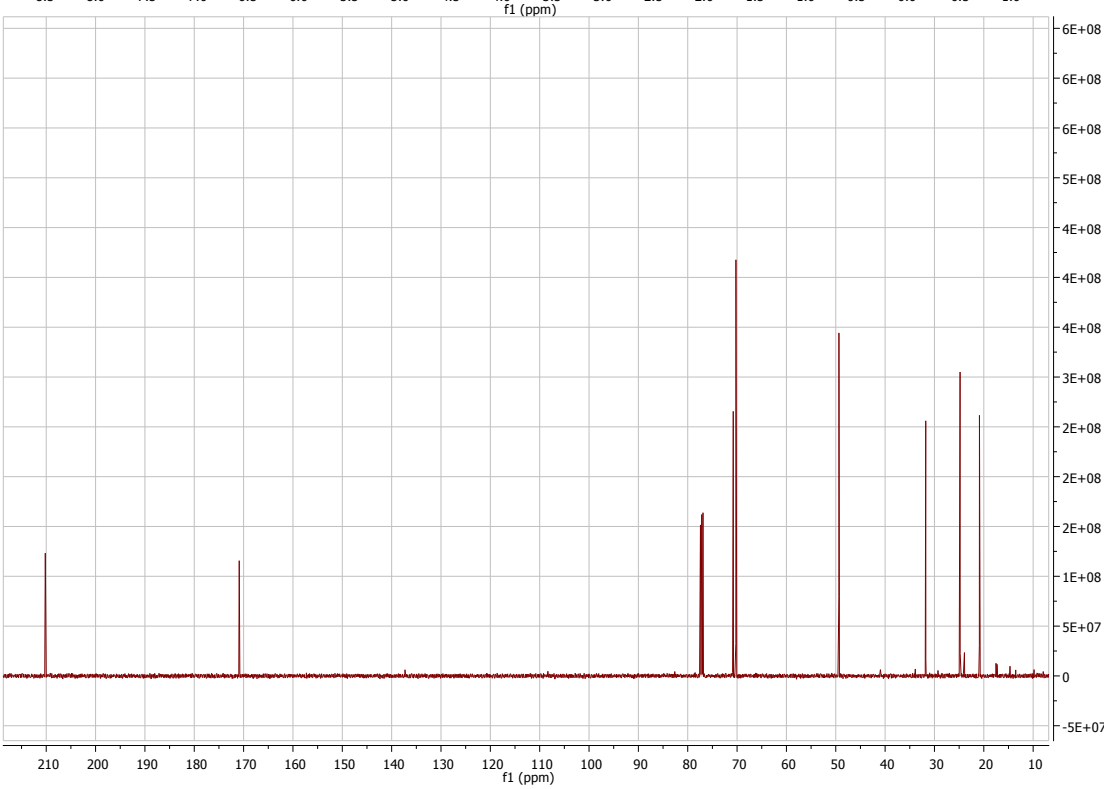


5. Copies of NMR-spectra

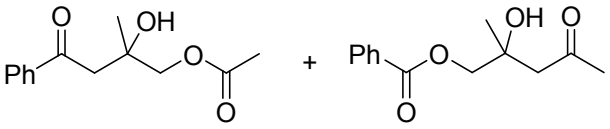
2-Hydroxy-2-methyl-4-oxopentyl acetate (**3a**)

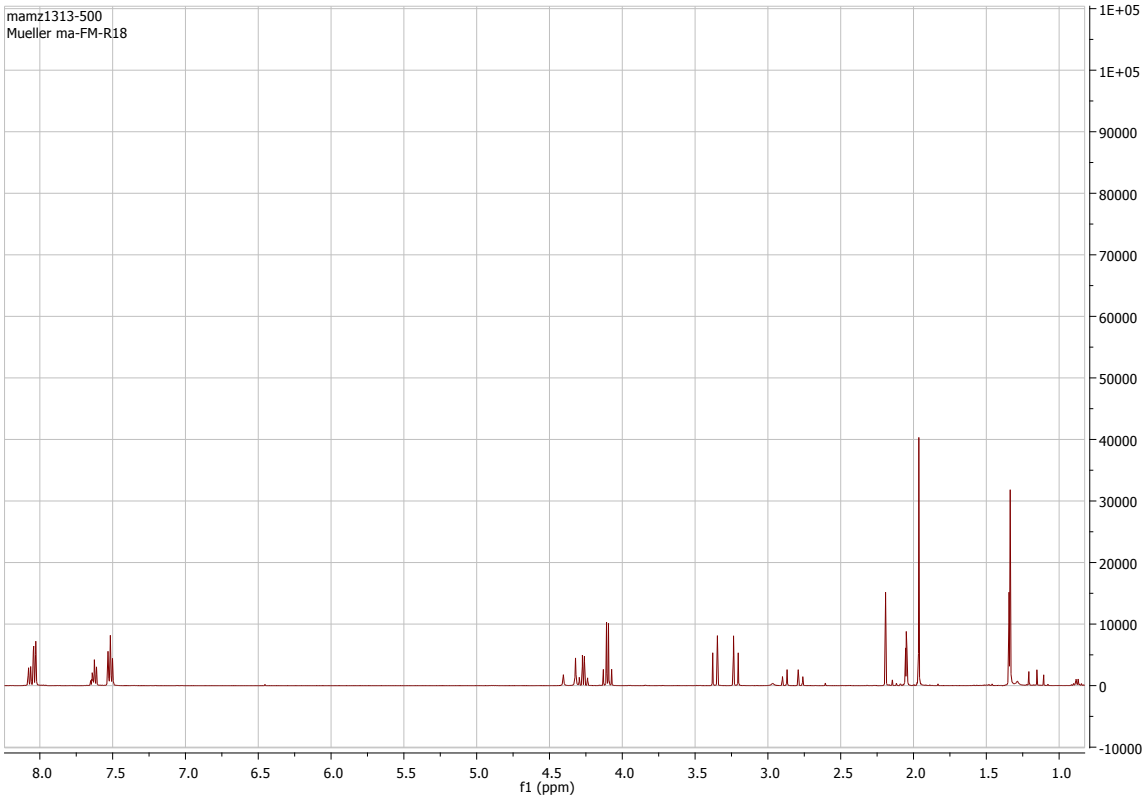


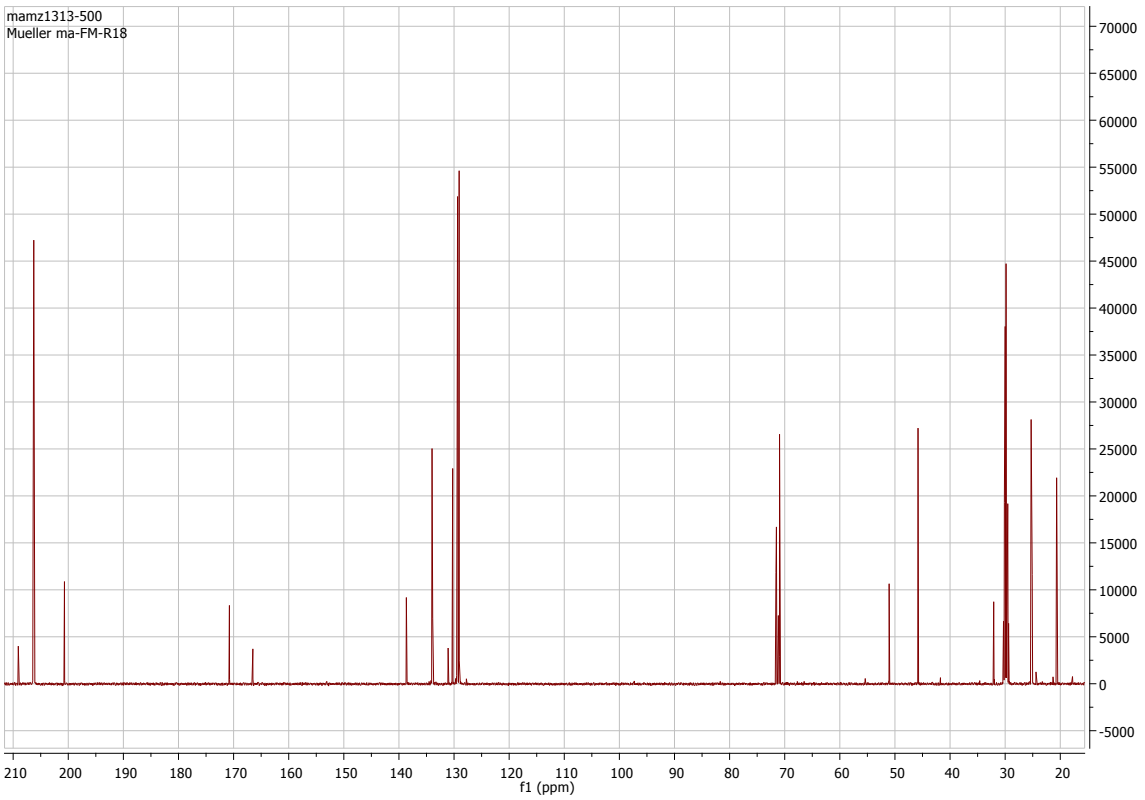




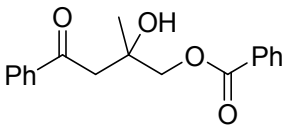
rac-2-hydroxy-2-methyl-4-oxo-4-phenylbutyl acetate (**3b**) and benzoate (**4b**)

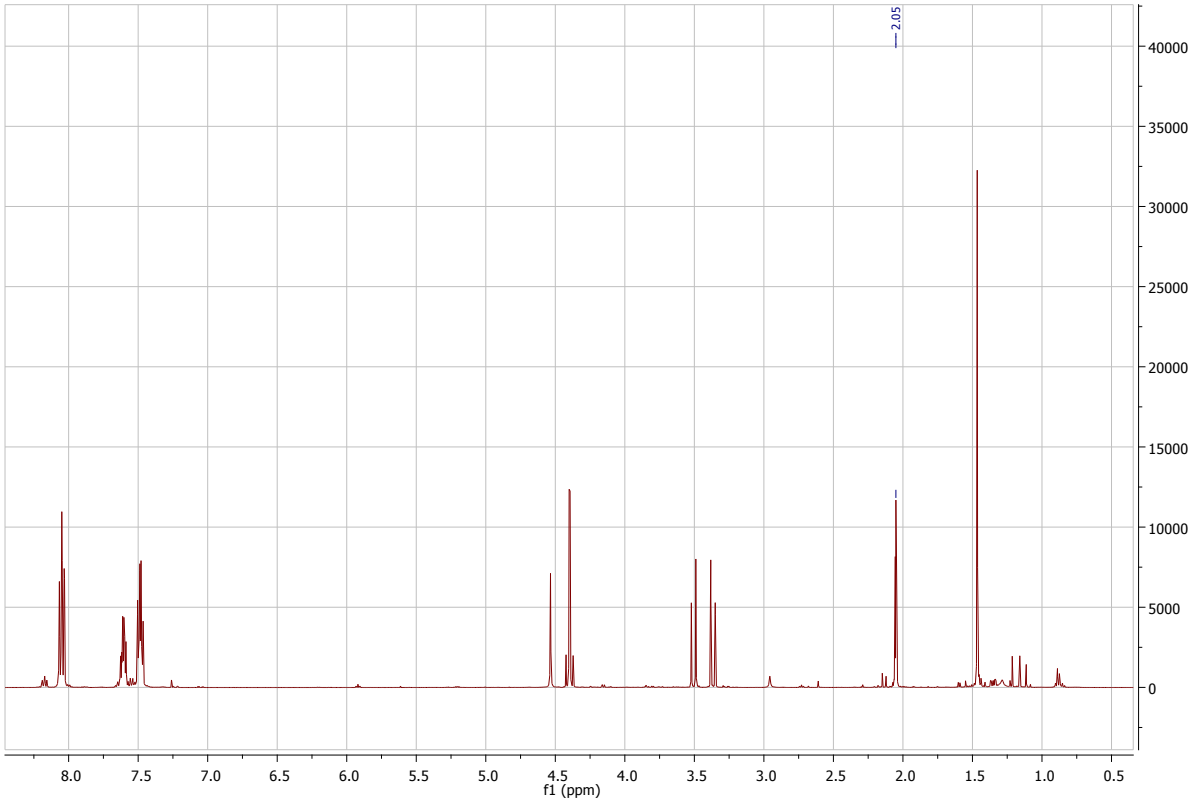


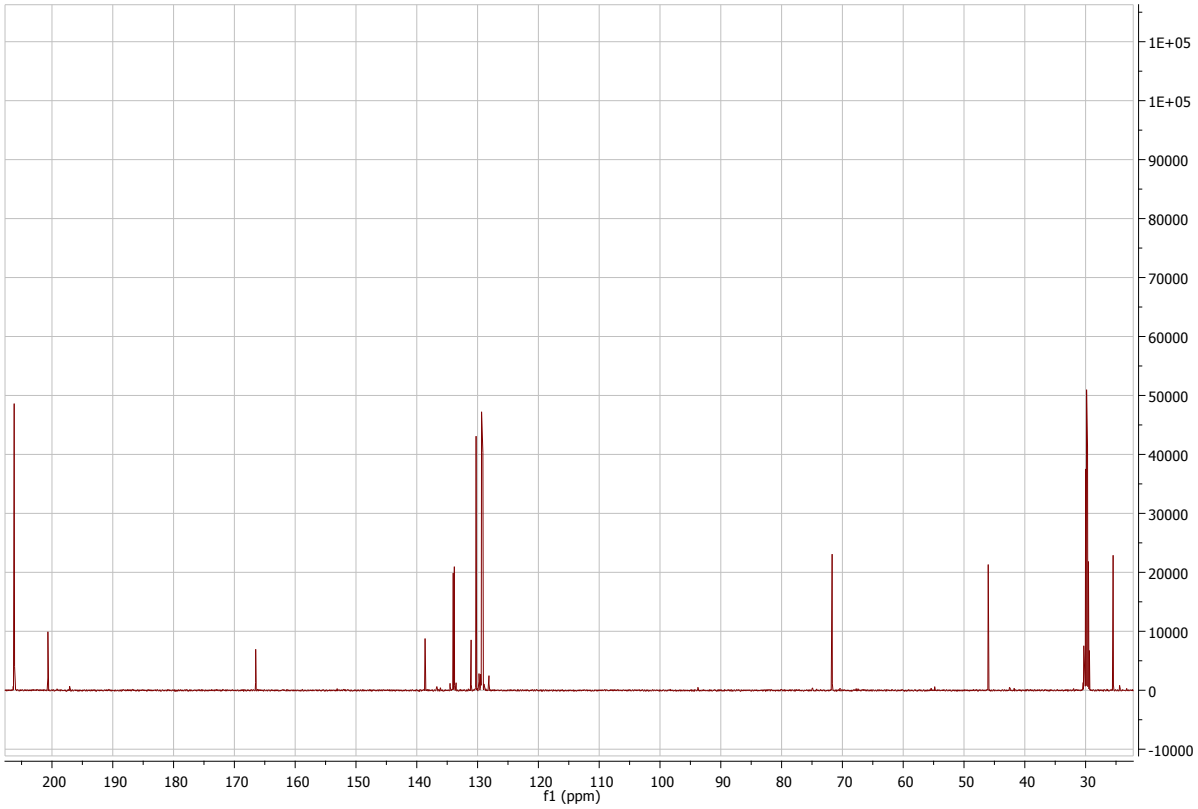




rac-2-hydroxy-2-methyl-4-benzoyl-butyl benzoate (**3c**)

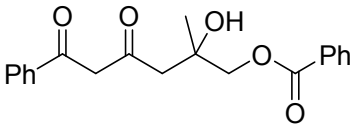


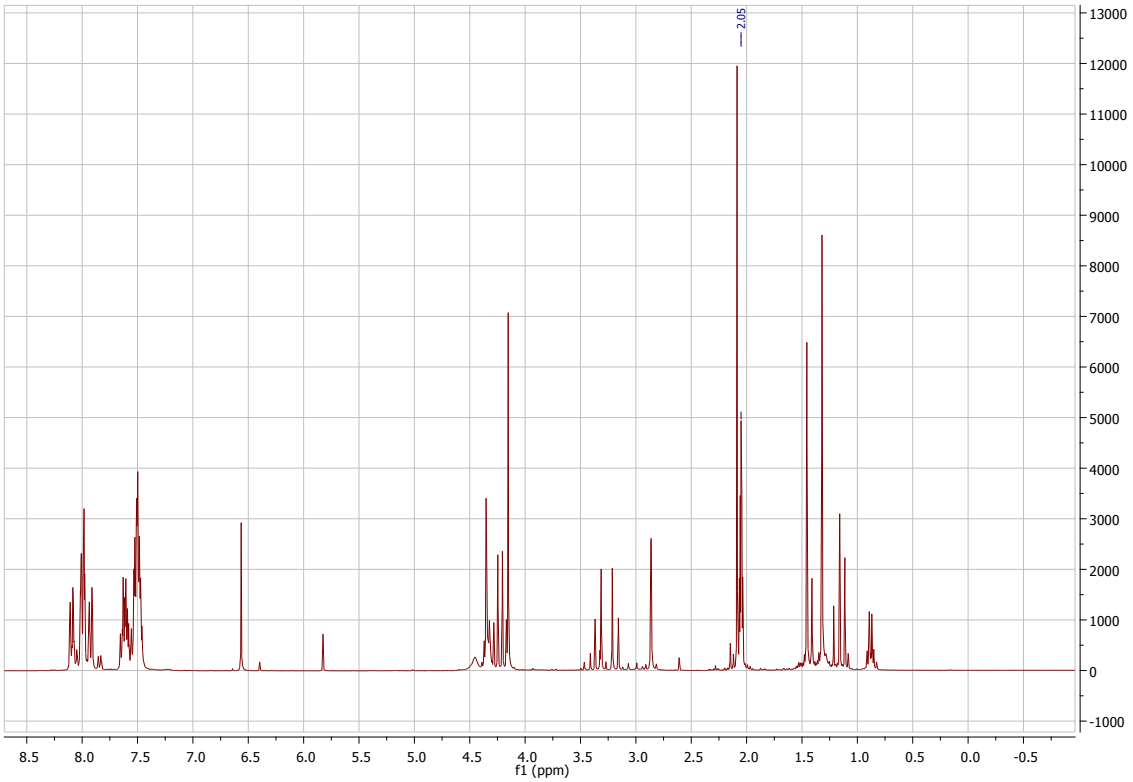


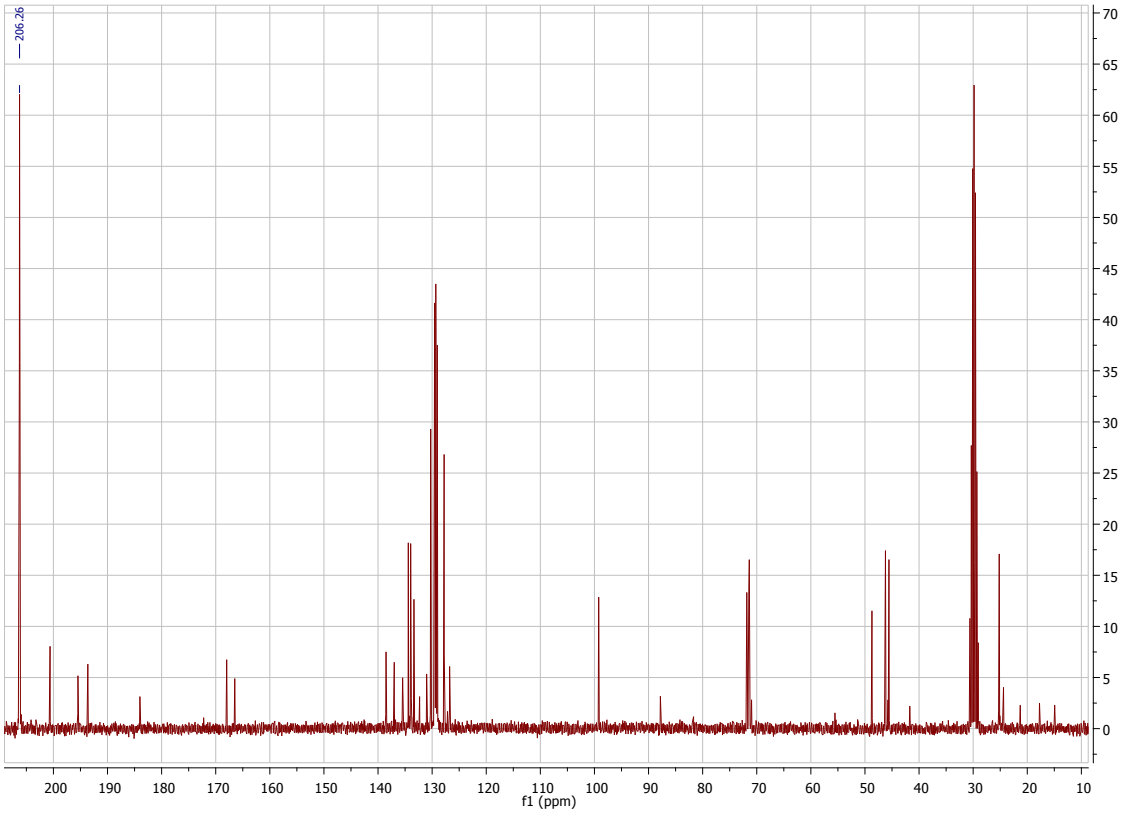


rac-2-hydroxy-2-methyl-4,6-dioxo-6-phenylhexyl benzoate (**3d**)

mixture of keto-enol-form (58/42)

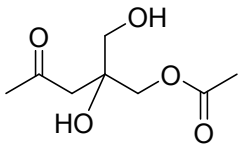


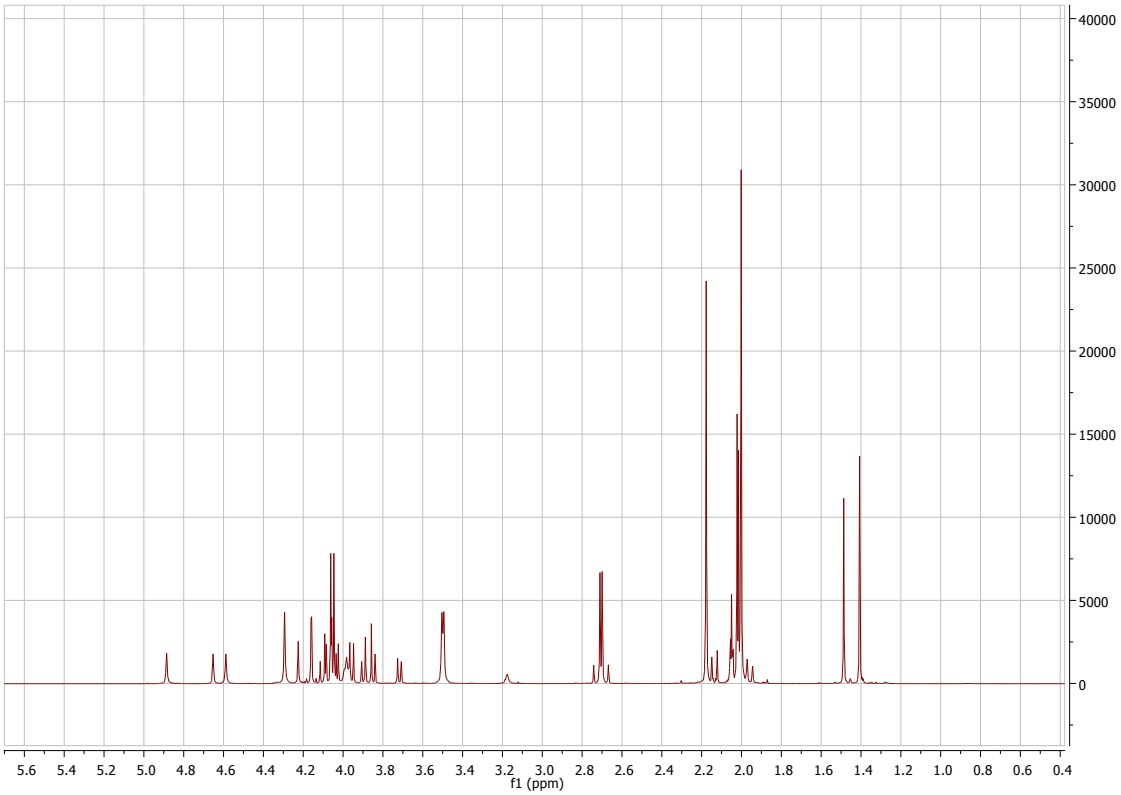


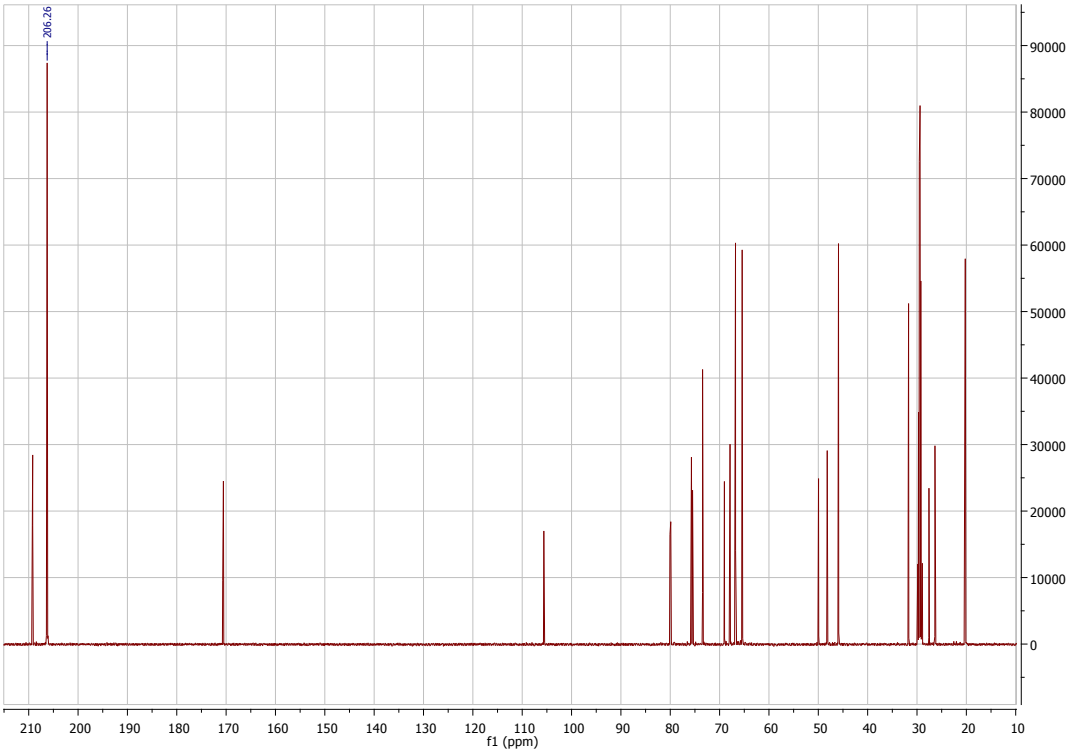


rac-2-hydroxy-2-(hydroxymethyl)-4-oxopentyl acetate (**6a**,**7a** and **7b**)

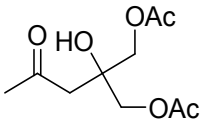
Mixture of open-alpha-beta-form (open/alpha/beta: 55/25/20).

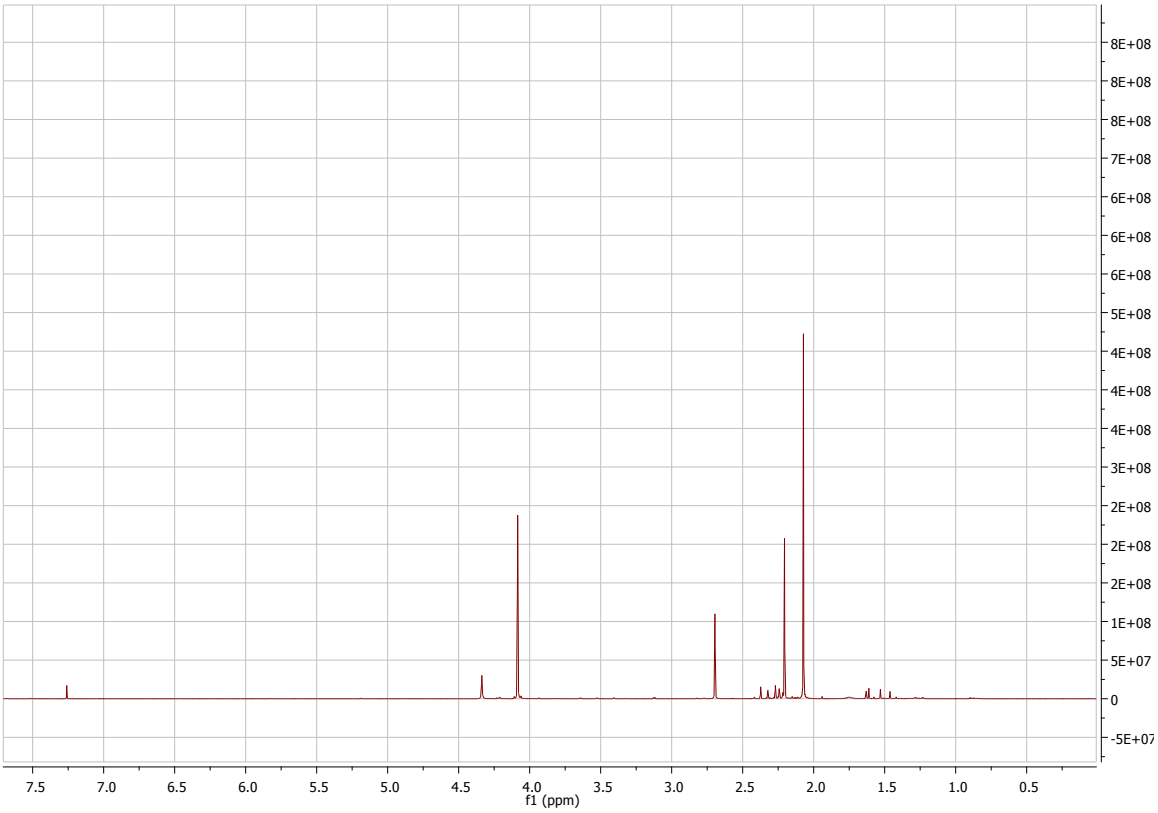


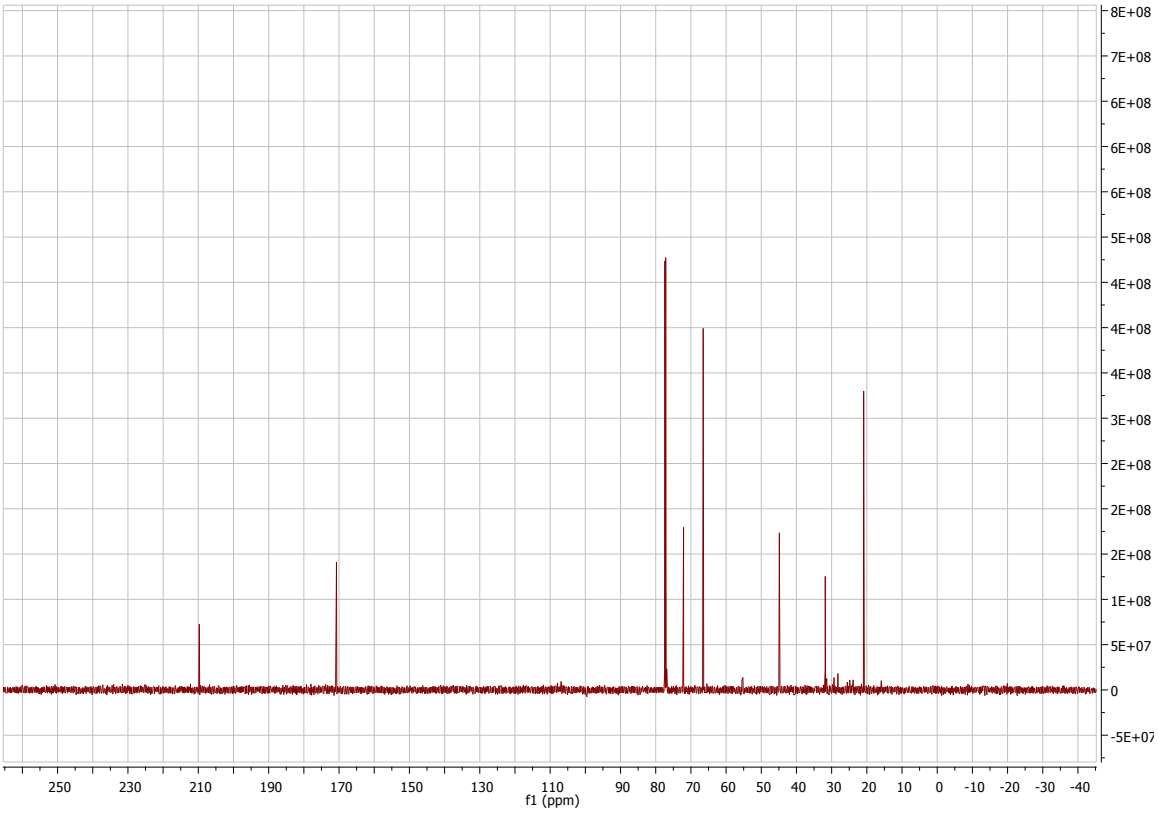




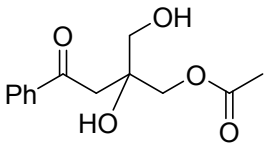
4,5-diacetoxy-4-(hydroxymethyl)pentan-2-one (diacetate of **6a**)

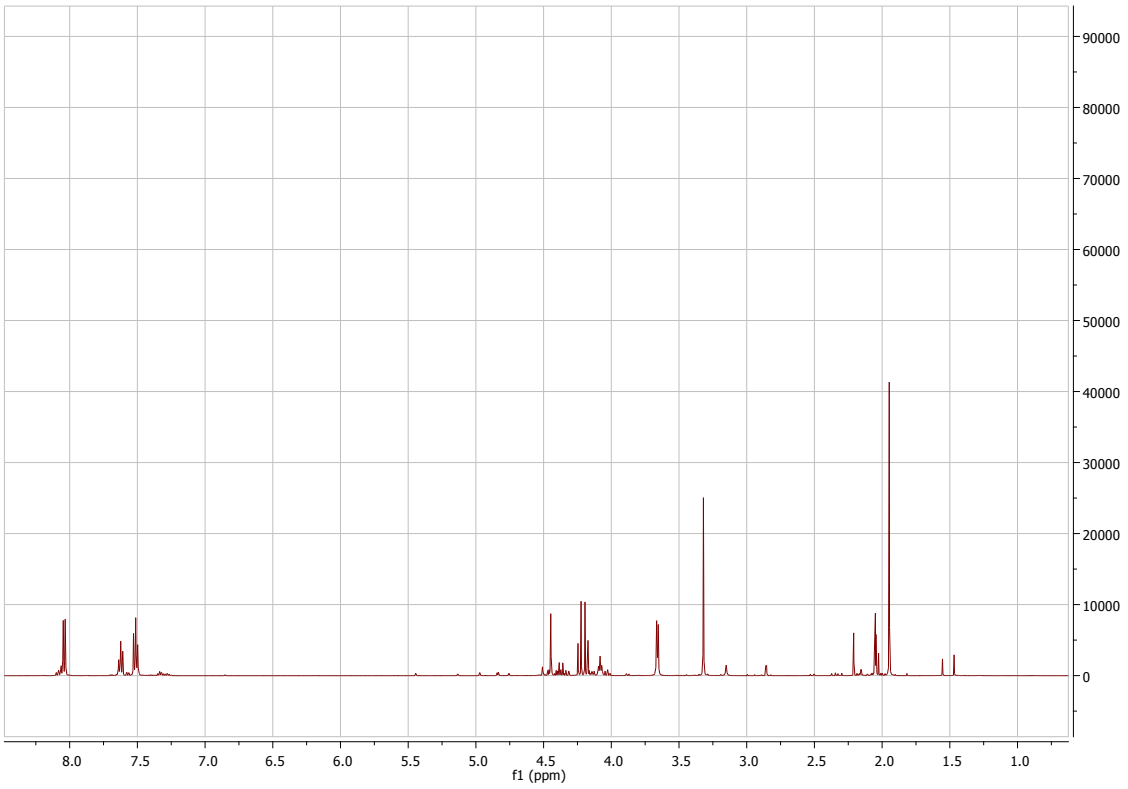


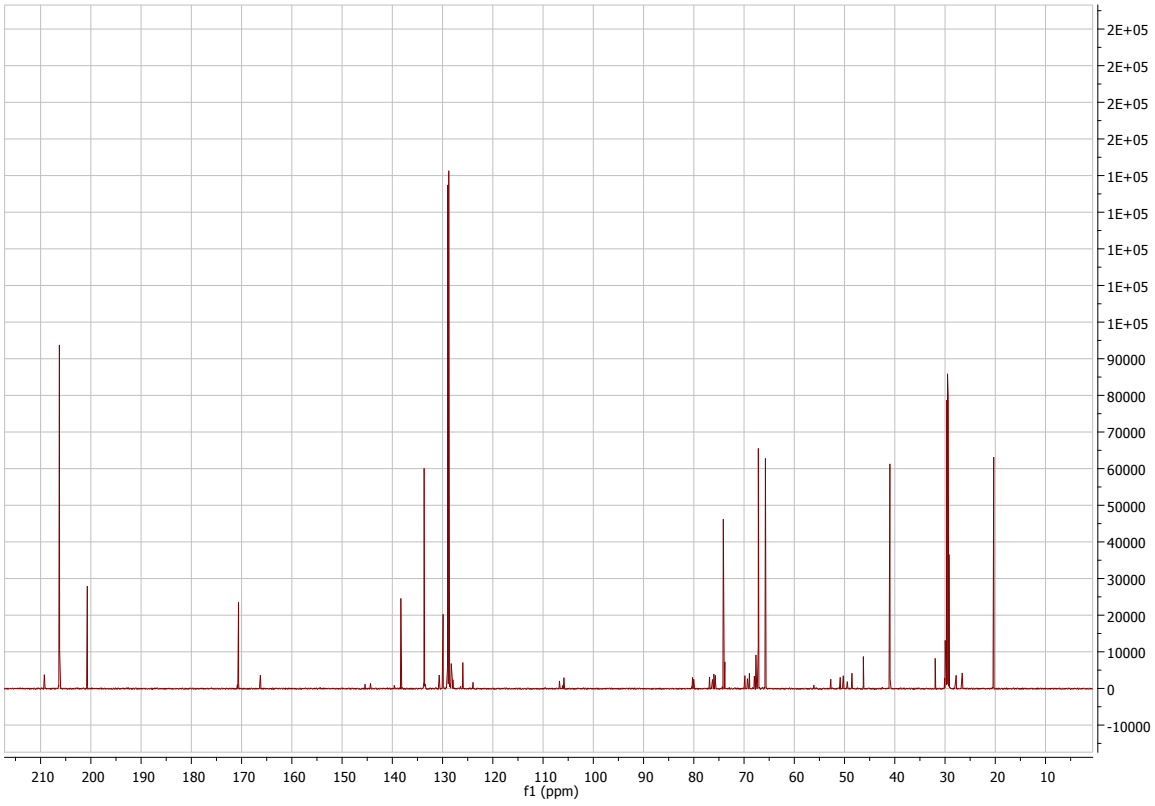




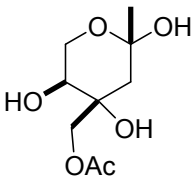
rac-2-hydroxy-2-(hydroxymethyl)-4-oxo-4-phenylbutyl acetate (**6b**)

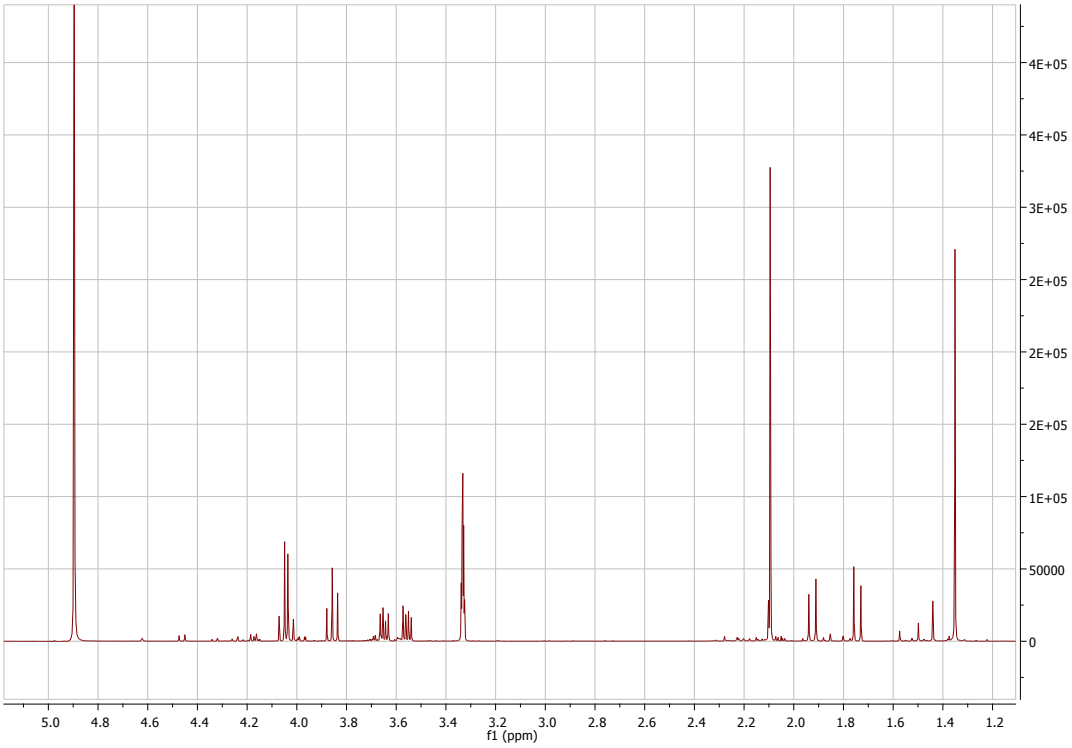


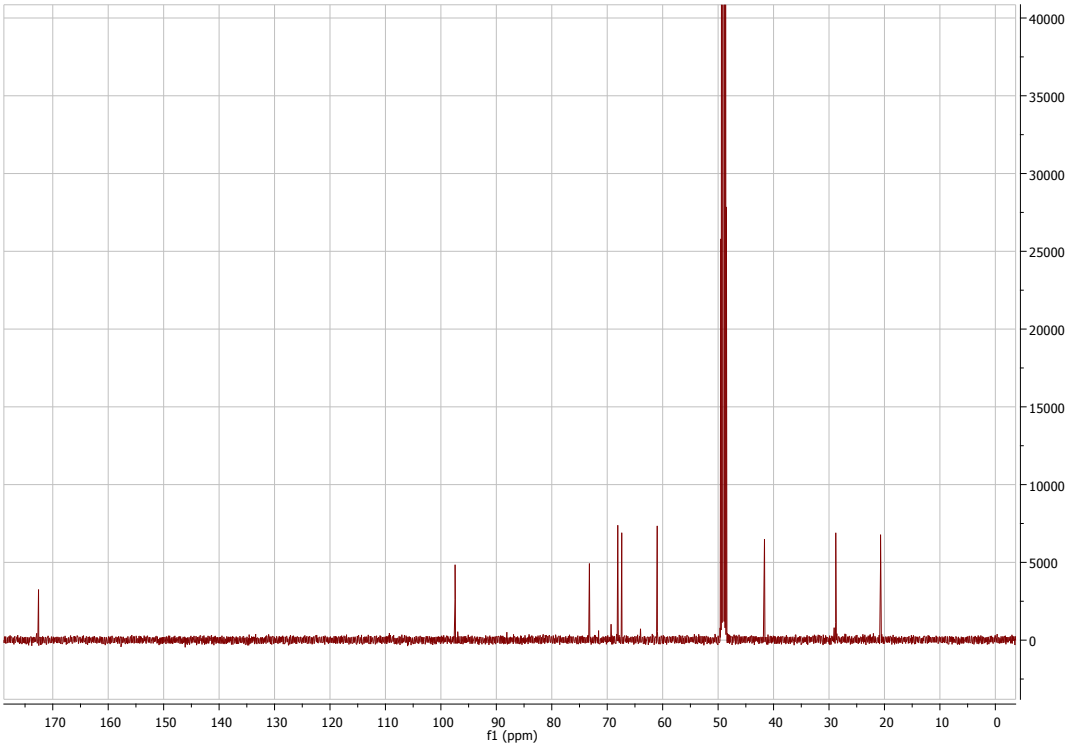




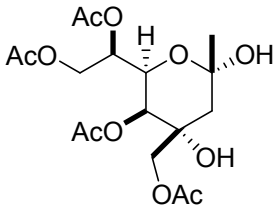
rac-((2S,4S,5S)-tetrahydro-2,4,5-trihydroxy-2-methyl-2H-pyran-4-yl)methyl acetate (**9**)

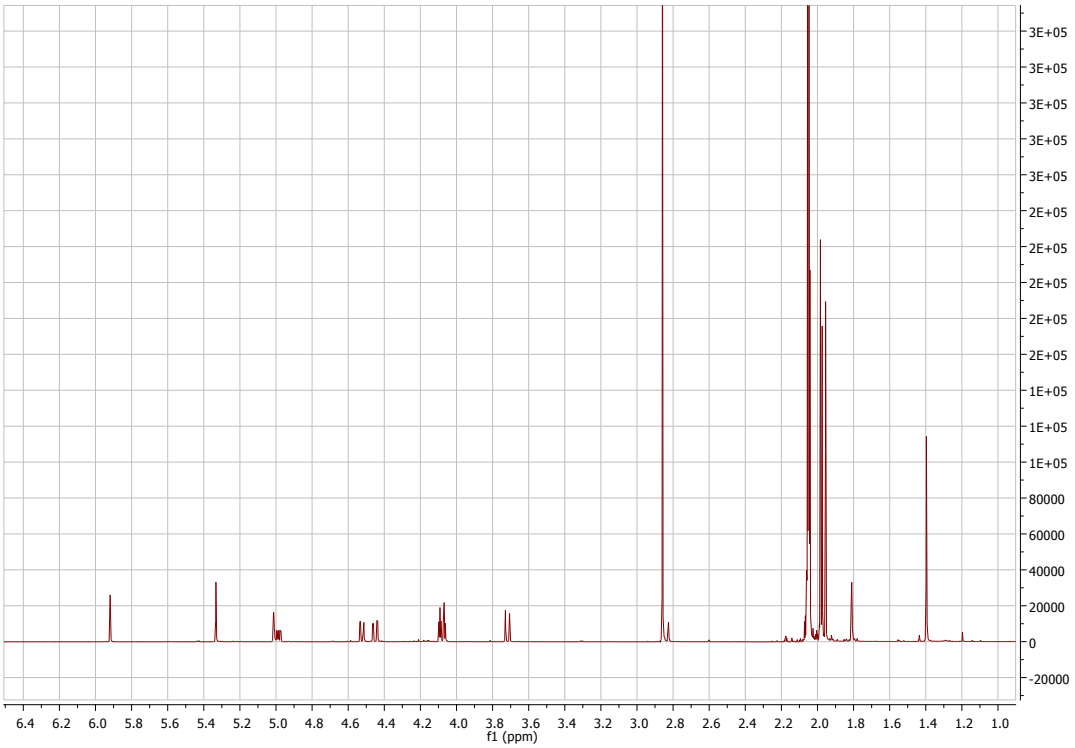


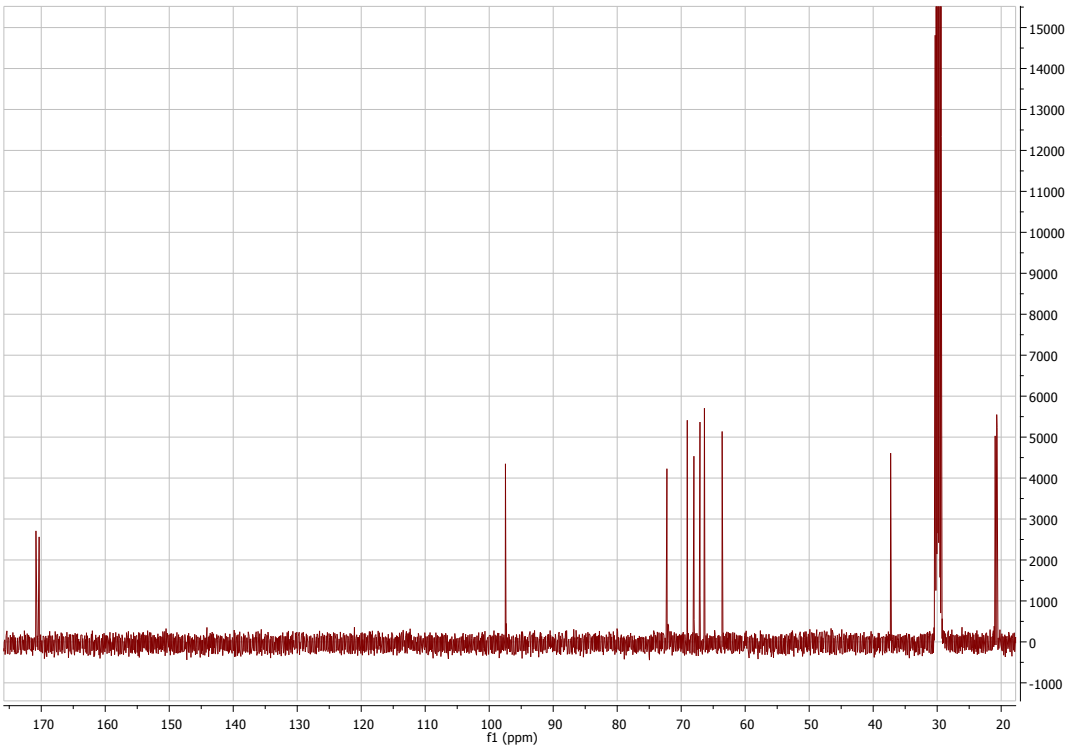




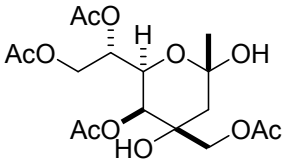
((2S,4R,5S,6R)-tetrahydro-2,4-trihydroxy-5-acetoxy-6-((R)-1,2-diacetoxyethyl)-2-methyl-2H-pyran-4-yl)methyl acetate (**13**)

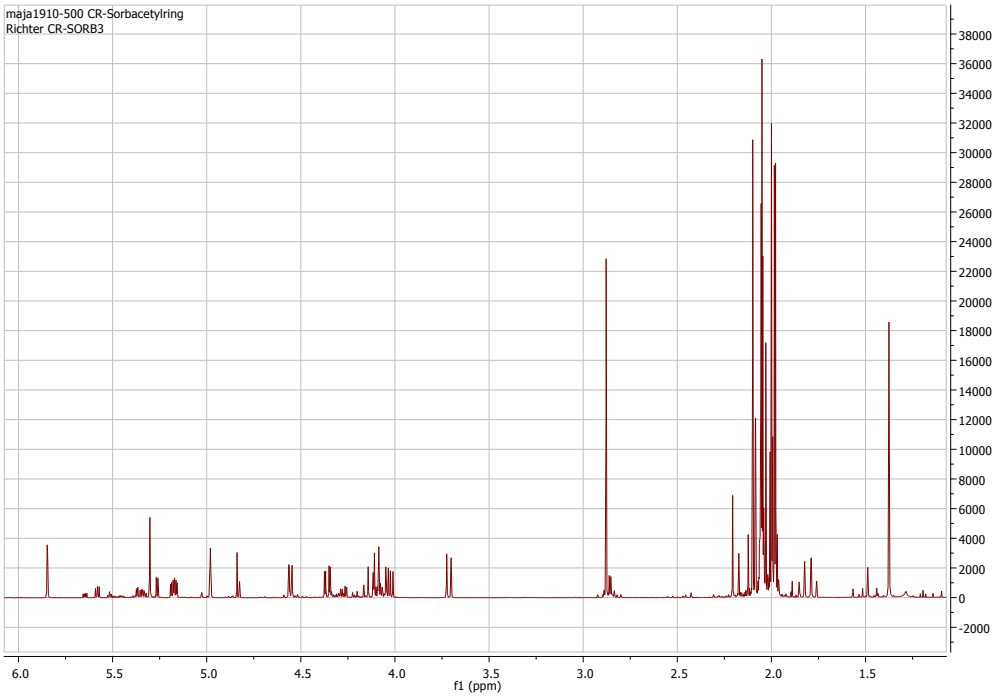


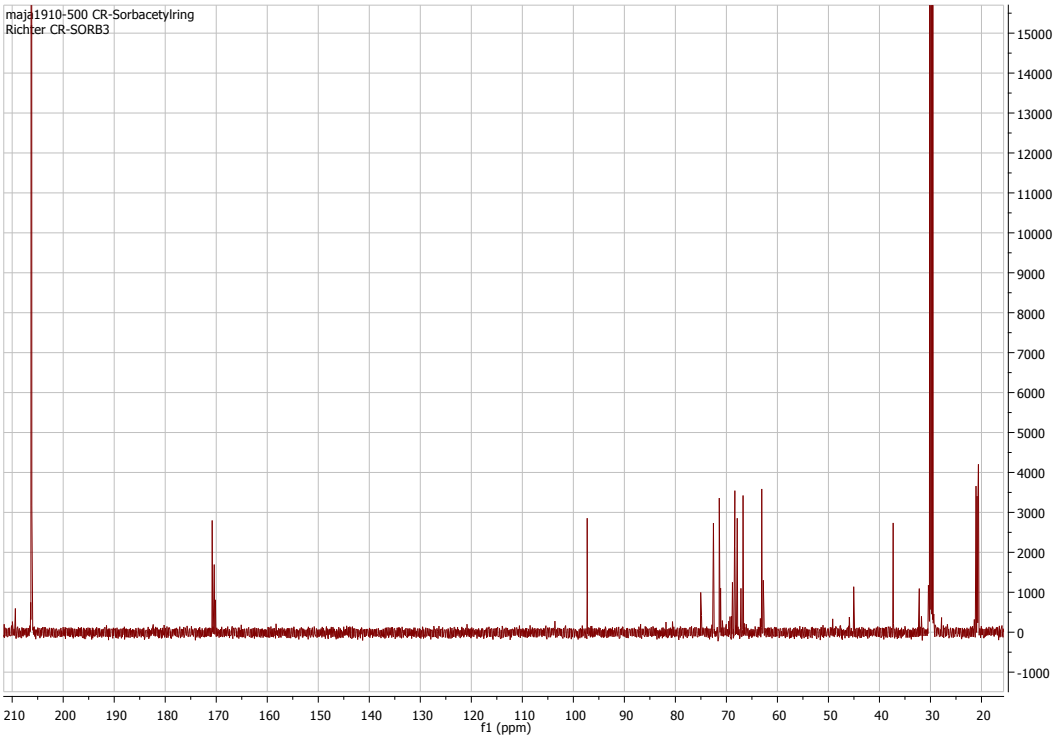




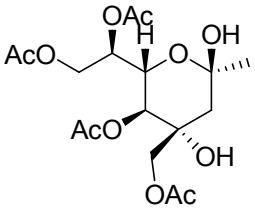
((2S,4R,5S,6R)-tetrahydro-2,4-trihydroxy-5-acetoxy-6-((S)-1,2-diacetoxyethyl)-2-methyl-2H-pyran-4-yl)methyl acetate (**14**)

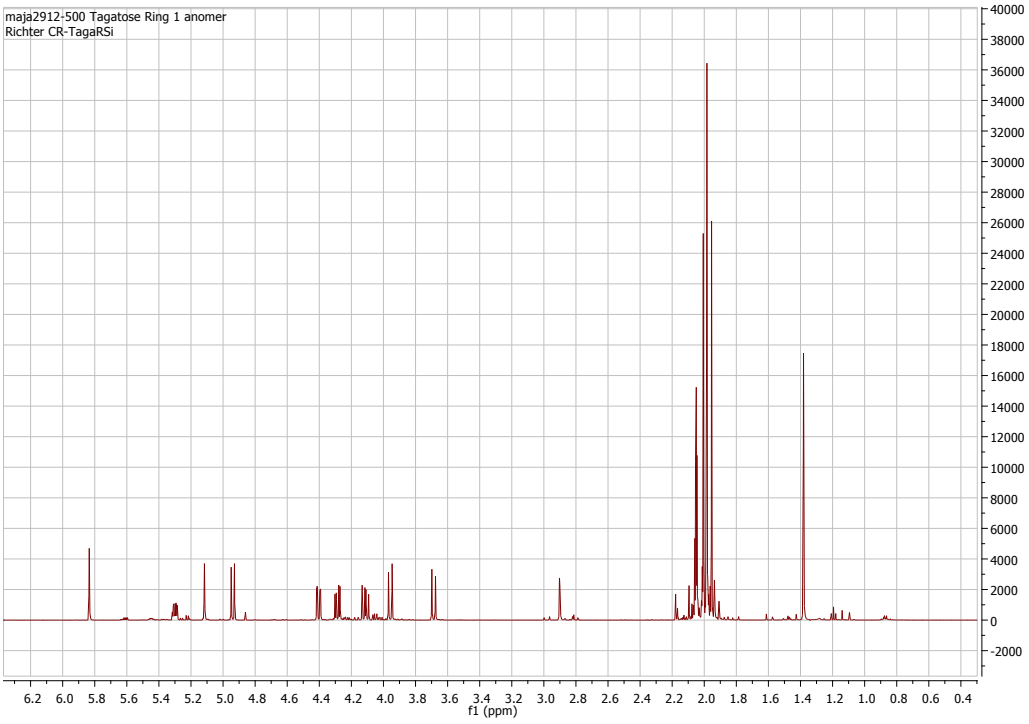


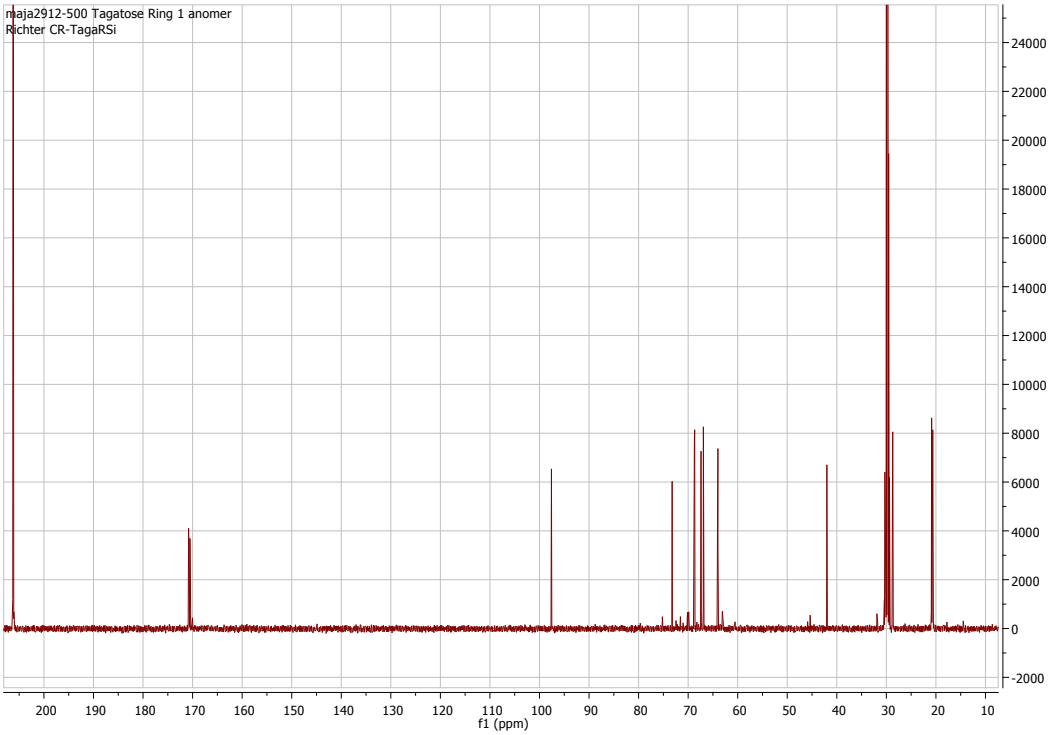




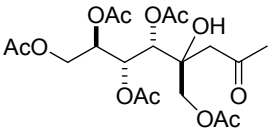
((2R,4R,5S,6S)-tetrahydro-2,4-dihydroxy-5-acetoxy-6-((R)-1,2-diacetoxyethyl)-2-methyl-2H-pyran-4-yl)methyl acetate (**15**)

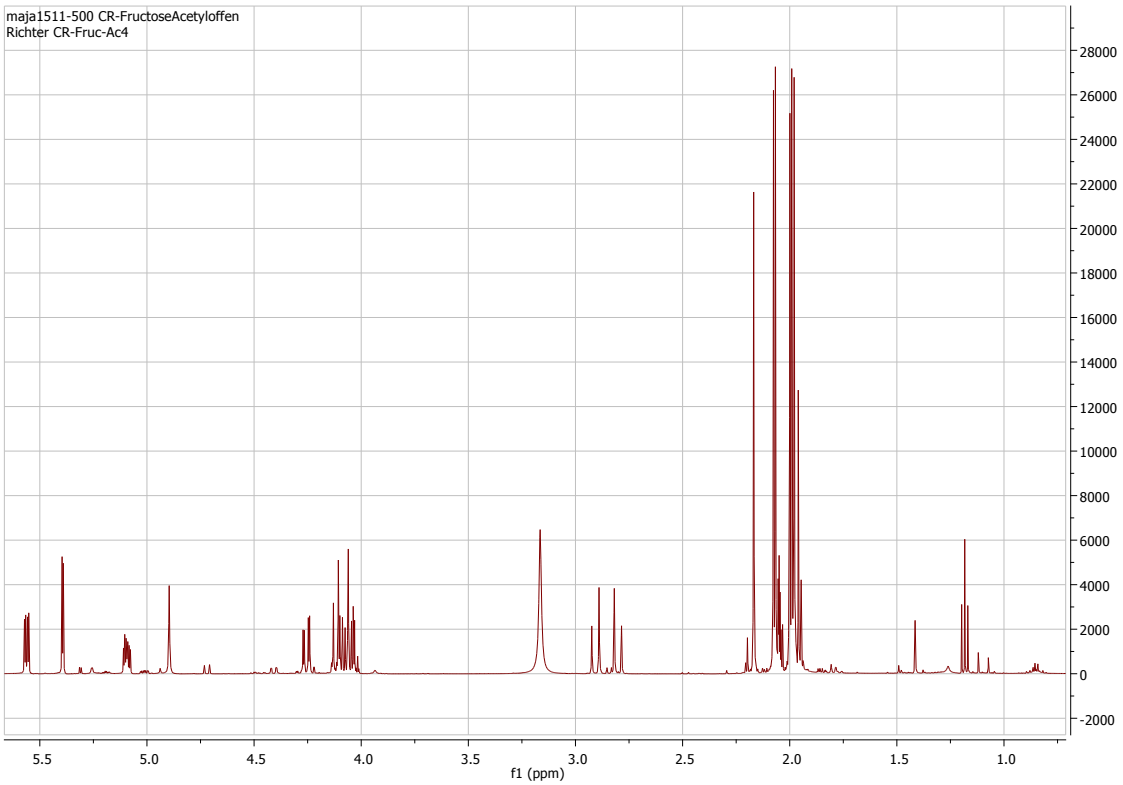


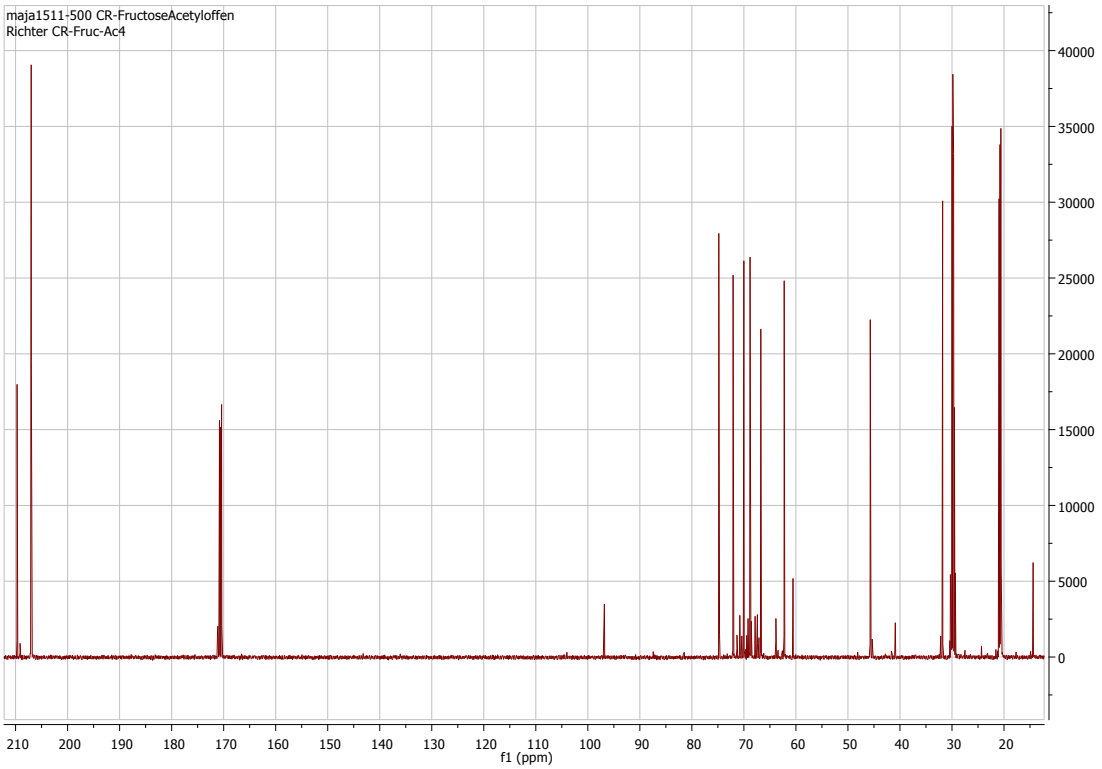




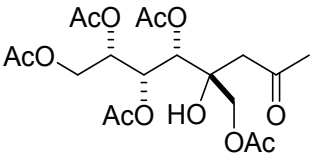
(4R,5S,6R,7R)-4,5,6,7,8-pentaacetoxy-4-(hydroxymethyl)octan-2-one (**16**)

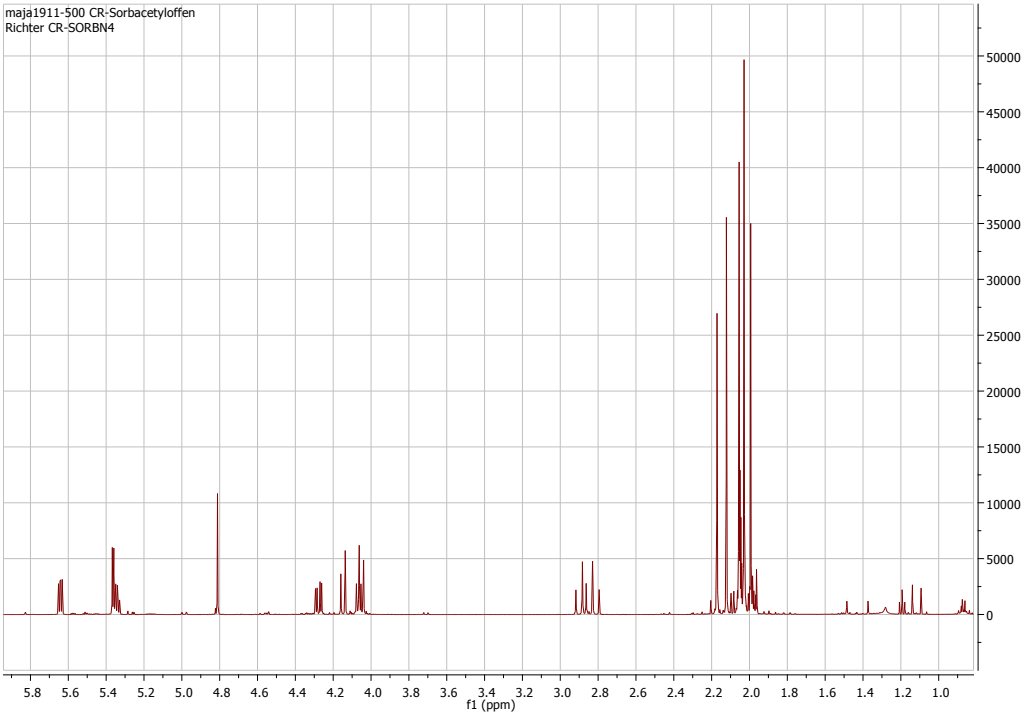


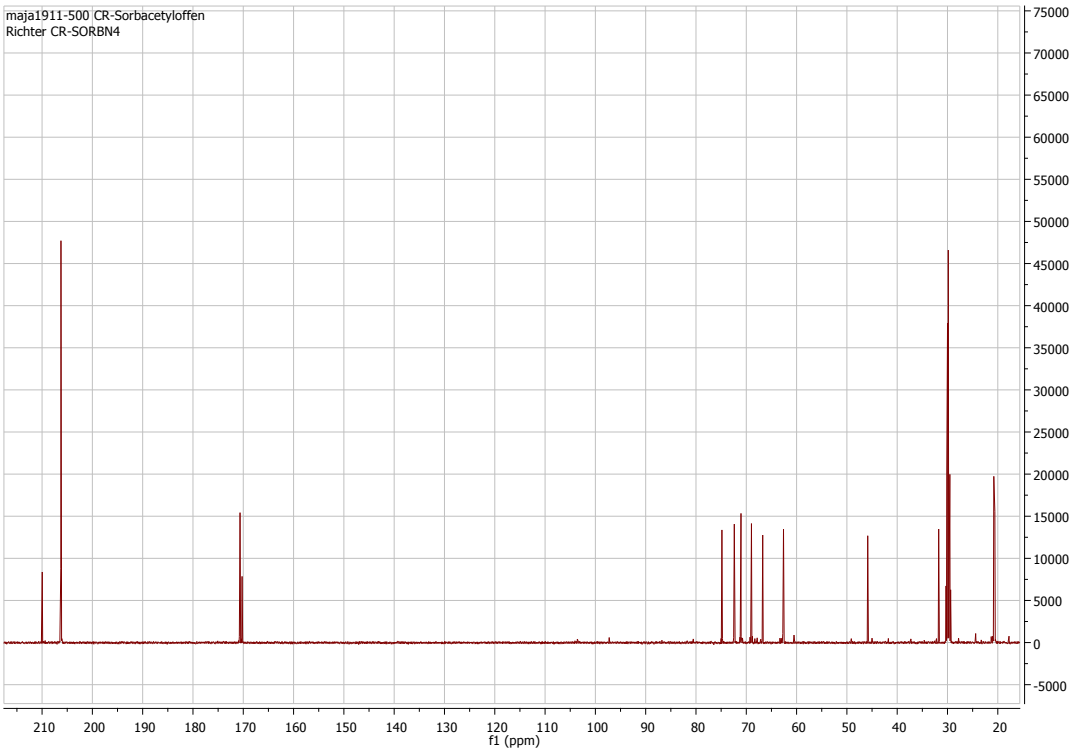




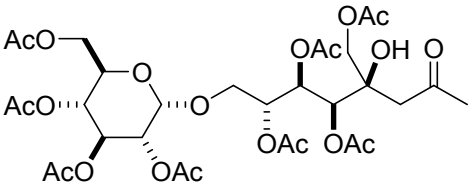
(4R,5S,6R,7S)-4,5,6,7,8-pentaacetoxy-4-(hydroxymethyl)octan-2-one (**17**)

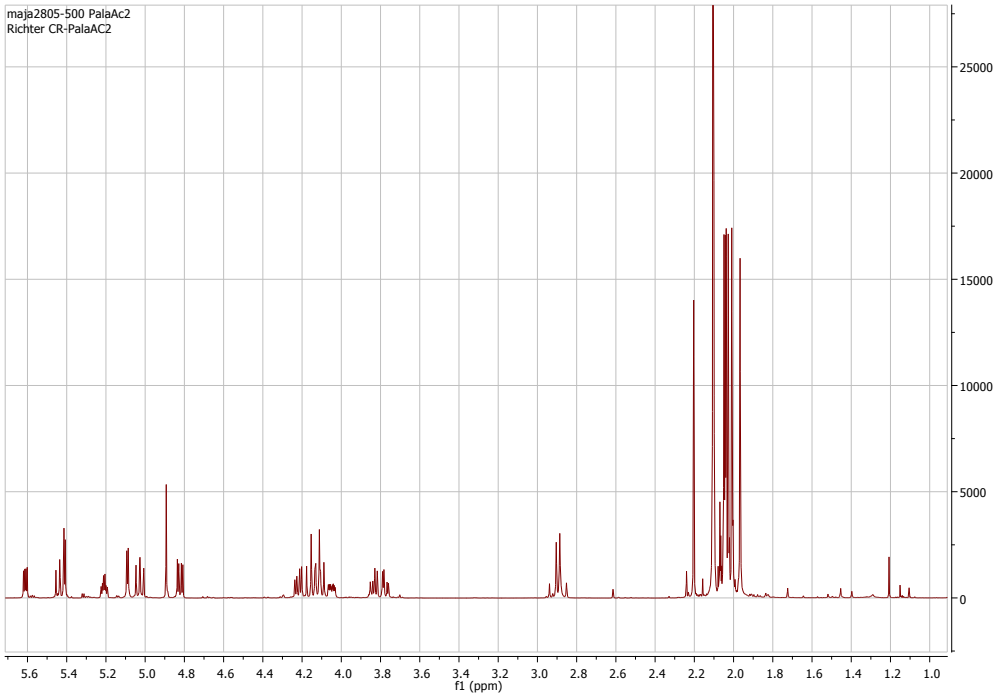


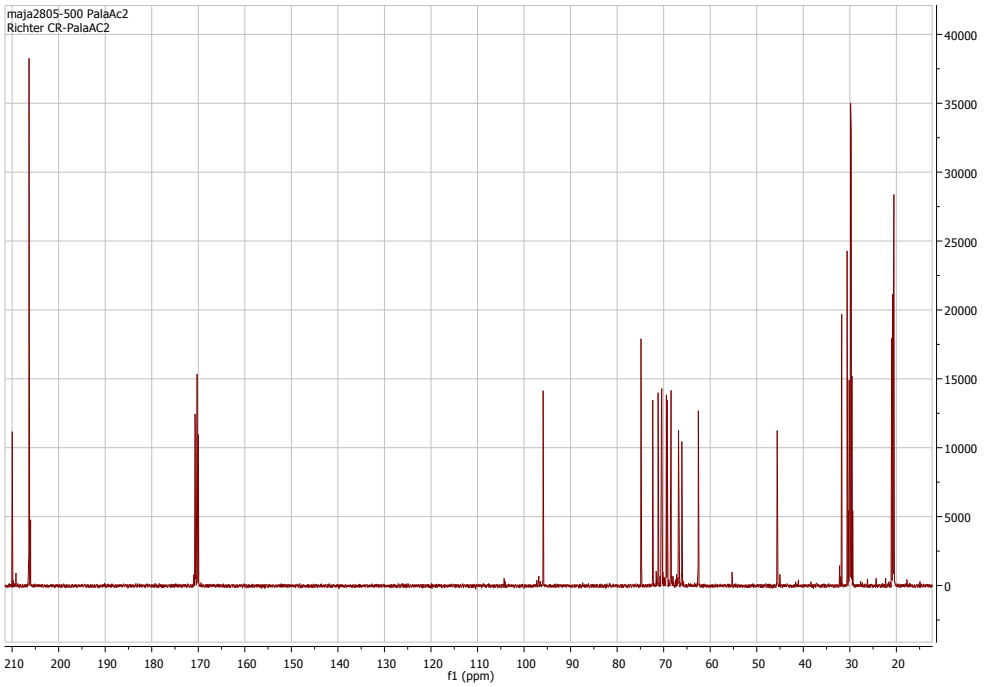




(4R,5S,6R,7R)-8-((2S,3R,4S,5S,6R)-tetrahydro-3,4,5-acetoxy-6-(acetoxymethyl)-2H-pyran-2-yloxy)-4-hyroxy-5,6,7-triacetoxy-4-(acetoxymethyl)octan-2-one (**18**)







6. References

1 Li, D. R.; Murugan, A.; Falck, J. R. *J. Am. Chem. Soc.* **2008,** *130*, 46-48